Advanced technologies for Piezoelectric Sensors in SHM systems: a review

Original Citation:

Advanced technologies for Piezoelectric Sensors in SHM systems: a review / L. Capineri. - ELETTRONICO. - (2021), pp. 28-28. (Intervento presentato al convegno SMS 2021 / EGF 2021 / Sensors 2021 / NanoMed 2021 joint conferences tenutosi a Milan , Italy nel 20-22 October 2021).

Availability:
This version is available at: 2158/1246083 since: 2021-10-26T14:22:12Z

Publisher:
MDPI

SMS 2021
SMART MATERIALS AND SURFACES

SENSORS 2021

EGF 2021
European Graphene Forum

NanoMed 2021

SMS / SENSORS / EGF / NANOMED 2021
JOINT HYBRID CONFERENCES

20 - 22 OCTOBER, 2021
MILAN, ITALY

BOOK OF ABSTRACTS

Organizer

SETCOR
Conferences & Exhibitions

SMS 2021 / Sensors 2021 / EGF 2021 / NanoMed 2021
Joint Hybrid Conferences Preliminary Program

20 - 22 October 2021 (GMT + 2 Time Zone for Onsite and Virtual Sessions)

Onsite Presentations Sessions

Wednesday, 20 Oct. 2021

08:00 - 12:00	Onsite Participant registration.	
Smart Materials and Surfaces - SMS 2021 Onsite Session I		
Onsite Conference Colonne A+B		
Session's Chairs: **Dr. Camilla Baratto, CNR-INO, PRISM Lab, Brescia, Italy** **Prof. Valentina Cauda, Polytechnic University of Turin, Italy**		
10:00 – 10:30	Thermomagnetic Energy Harvesting: From Material Properties to the Engineering of Functional Devices **M. Kohl**	**Prof. Manfred Kohl**, Karlsruhe Institute of Technology, **Germany**
10:30 - 10:45	Structures of ice confined in nanopores; pressure enhancement and wetting energy effects **M. Śliwinska-Bartkowiak**, M. Jazdzewska, K.Rotnicki, A.Beskrovny and K. E. Gubbins	**Prof. Malgorzata Sliwinska-Bartkowiak**, Adam Mickiewicz University, Poznan, **Poland**
10:45 – 11:00	The role of long-range electrostatic interactions and local topology of the hydrogen bond network in the wettability of fully and partially wetted single and multilayer graphene **M. Chiricotto**, F. Martelli, G. Giunta and P. Carbone	**Dr. Mara Chiricotto**, The University of Manchester, **UK**
11:00 - 11:15	Buckle depression as a signature of the elastic properties of 2D materials **C. Coupeau**	**Prof. Christophe Coupeau**, University of Poitiers, **France**
11:15 - 11:30	Tailor-Making Nano Insulation Materials through Synthesis of Hollow Silica Nanospheres **B. P. Jelle** and S. Alex Mofid	**Prof. Bjørn Petter Jelle** Norwegian University of Science and Technology **Norway**
11:30 - 11:45	Viologen π-Dimerization as a Trigger for Metamorphism in Supramolecular Stimuli-Responsive Materials **D. Frath**, T. Gibaud, S. Chowdhury, C. Kahlfuss, C. Roizard, A. F. Carreira, R. Grüber, Y. Nassar, L. Guy, F. Chevallier, E. Dumont, A. P. Ramos, G. J.-F. Demets, E. Saint-Aman and C. Bucher	**Dr. Denis Frath**, CNRS- ENS Lyon, **France**
11:45 - 12:00	Analytical, Numerical and Experimental Study of the Self-Heating of a Shape Memory Composite **C. A. Pereira Sánchez**, M. Houbben, J. F. Fagnard, P. Laurent, C. Jérôme, L. Noels and P. Vanderbemden	**Ms. Clara. A. Pereira Sánchez**, University of Liège, **Belgium**
12:00 - 14:00	**Lunch Break**	
Session's Chairs: **Prof. Manfred Kohl, Karlsruhe Institute of Technology, Germany** **Prof. Malgorzata Sliwinska-Bartkowiak, Adam Mickiewicz University-Poznan, Poland**		
14:00 - 14:30	Martensitic microstructures in nanocrystalline NiTi wires thermomechanically loaded in tension **P. Šittner**, O.Molnárová, L.Heller and H.Seiner	**Dr. Petr Sittner**, Czech Academy of Sciences, **Czech Republic**
14:30 - 14:45	Landau-energy Landscape Reconstruction for a Ni-Fe-Ga(Co) Shape Memory Alloy **H. Seiner**, K. Zoubková, P. Sedlák, E. Villa, M. Tahara, H. Hosoda and V. Chernenko	**Prof. Hanus Seiner**, Institute of Thermomechanics- Czech Academy of Sciences, **Czech Republic**
14:45 - 15:00	Localization of Martensitic Transformation in NiTi Shape Memory Alloys: Experimental Observations by 3D Diffraction/Scattering Computed Tomography and Numerical Reconstruction **P. Sedlak**, M. Frost, H. Seiner and P. Sittner	**Dr. Petr Sedlak**, Institute of Thermomechanics- Czech Academy of Sciences, **Czech Republic**

15:00 - 15:15	Ultrasonic-based evaluation of the NiTi shape-memory alloy elasticity during stress-induced martensitic transformation **T. Grabec**, P. Sedlák, K. Zoubková, P. Stoklasová, M. Ševčík, M. Janovská and H. Seiner	**Dr. Tomáš Grabec**, Institute of Thermomechanics- Czech Academy of Sciences, **Czech Republic**
15:15 - 15:30	Correlation between microstructural condition and functional and magnetic properties in sintered Ni50Mn30Ga20 ferromagnetic shape memory alloy **F. Villa**, A. Nespoli, C. Fanciulli, F. Passaretti, F. Albertini and E. Villa	**Dr. Francesca Villa**, CNR ICMATE Unit of Lecco, **Italy**
15:30 - 15:45	Elastocaloric properties of polycrystalline samples of NiMnGaCu ferromagnetic shape memory alloy in compression configuration **E. Villa**, C. Tomasi, F. Villa, E. Bestetti, A. Nespoli and F. Passaretti	**Dr. Elena Villa**, National Resarch Council CNR ICMATE Unit of Lecco, **Italy**
15:45 - 16:00	Magnetic and Dielectric Properties of Ruddlesden–Popper Ca3Mn2O7 thin films prepared by Pulsed Laser Ablation **B. Silva**, J. Oliveira, T. Rebelo, P. Rocha-Rodrigues, N. Lekshmi, A. Lopes, J. Araújo, L. Francis and B. Almeida	**Ms. Bruna Silva**, Minho University, Braga, **Portugal**
16:00 - 16:30	**Afternoon Coffee Break**	
Session's Chairs: **Prof. Hanus Seiner, Institute of Thermomechanics - Czech Academy of Sciences, Czech Republic** **Dr. Alberto Jimenez-Suarez, Rey Juan Carlos University, Spain**		
16:30 - 16:45	Analysis of Changes of Wood Color, Mass, Density and Total phenolic compounds after thermal treatment process M. Aleinikovas, **B. Šilinskas**, M. Škėma, I. Varnagirytė-Kabašinskienė and L. Beniušienė	**Dr. Benas Šilinskas**, Lithuanian Research Centre for Agriculture and Forestry, **Lithuania**
16:45 - 17:00	Emergent Opto-Electronic Properties in Molecular-Metal Polymer Nanocomposites **R. Pfattner**, E. Laukhina, M. Mas-Torrent, V. Laukhin, C. Rovira and J. Veciana	**Dr. Raphael Pfattner**, Materials Science Institute of Barcelona (ICMAB-CSIC), **Spain**
17:00 - 17:15	Multiply Positively Charged Cyclodextrin Derivatives Usable for Stable Modification of Negatively Charged Solid Support **J. Jindřich** and P. Kasal	**Prof. Jindrich Jindrich**, Charles University- Prague, **Czech Republic**
17:15 - 17:30	Microgels as "on demand" Cation Release Systems **V. Chimisso**, S. Conti, P. Kong, C. Fodor, and W. Meier	**Ms. Vittoria Chimisso**, University of Basel, **Switzerland**
17:30 - 17:45	Smart polymer nanocomposites I. Lorero, M. Campo, A. Jiménez-Suárez and **S. G. Prolongo**	**Dr. Silvia Gonzalez Prolongo**, Rey Juan Carlos University, **Spain**
17:45 - 18:00	Smart nanocomposites based on thermoset polymers reinforced with carbon nanostructures **A. Jiménez-Suárez**, V. Martínez-Martínez, M.I. Rodríguez-Tapiador, X.X.F. Sánchez-Romate and S.G. Prolongo	**Dr. Alberto Jimenez-Suarez**, Rey Juan Carlos University, **Spain**
18:00 - 18:15	Electrical, thermo-electrical and electro-magnetical behaviour of graphitic nanofillers/epoxy nanocomposites I. Collado, A. Jiménez-Suárez, **G. Del Rosario** and S. G. Prolongo	**Dr. Gilberto Del Rosario**, Rey Juan Carlos University, **Spain**

Thursday, 21 October 2021

Smart Materials and Surfaces 2021 / Sensors 2021 Joint Onsite Session I		
Onsite Conference Colonne A+B		
Session's Chairs: **Prof. Mamas Prodromidis, University of Ioannina, Greece** **Prof. Stefano Cinti, University of Naples Federico II, Italy**		
09:00 - 09:30	Advances in light activated gas sensors based on ZnO nanowires G. Ambrosio, T.T. Le Dang, D. Rocco2, C. De Angelis, G. Faglia and **C. Baratto**	**Dr. Camilla Baratto**, CNR-INO, PRISM Lab, Brescia, **Italy**
09:30 - 10:00	Multi-functionalized silica nanoparticles to improve the sensitivity of diagnostic assays **C. Chaix**, C. Farre, M. Manzano and J. Vidic	**Prof. Carole Chaix**, Claude Bernard University Lyon 1, **France**
10:00 - 10:30	Can chemometrics tool improve development of electrochemical paper-based devices? **S. Cinti**	**Prof. Stefano Cinti**, University of Naples Federico II, **Italy**
10:30 - 11:00	**Morning Coffee Break**	
11:00 - 11:30	Advanced technologies for Piezoelectric Sensors in SHM systems: a review **L. Capineri**	**Prof. Lorenzo Capineri**, University of Florence, **Italy**
11:30 - 11:45	Molecularly Imprinted Polymer Capacitive Chemosensor for Determination of Heterocyclic Aromatic Amines **V. Ayerdurai**, A. Garcia-Cruz, M. Cieplak, P.S. Sharma, F. D`Souza and W. Kutner	**Ms. Viknasvarri Ayerdurai**, Institute of Physical Chemistry, **Poland**
11:45 - 12:00	Challenges for a High Temperature Glass Solder for the Assembly Concept of a Piezoelectric Resonator **F. Kohler**, M. Schulz, H. Fritze and J. Wilde	**Mr. Fabian Pascal Kohler**, University of Freiburg, **Germany**
12:00 - 12:15	Metal nanoparticles decorated graphene for the development of gas sensors dedicated to sulfur-containing pollutants **E. Ruiz**, T. Gueye, C. Varenne, A. Ndiaye, J. Brunet and A. Pauly	**Ms. Elisa Ruiz**, CNRS-Clermont Auvergne University, **France**
12:15 - 12:30	Ultra hight sensitive NO2 gas microsensor for environmental monitoring or mapping urban air quality **T. Gueye**, J. Brunet, A. Ndiaye, C. Varenne, E. Ruiz and A. Pauly	**Mr. Thiaka Gueye**, CNRS-Clermont Auvergne University, **France**
12:30 - 12:45	Transmissibility estimation of a metamaterial-based decoupling device for vibration measurement A. Annessi, P. Chiariotti, V. Zega, M.Martarelli and P.Castellini	**Mr. Alessandro Annessi**, Marche Polytechnic University, **Italy**
12:00 - 14:00	**Lunch Break**	
Session's Chairs: **Dr. Camilla Baratto, CNR-INO, PRISM Lab, Brescia, Italy** **Prof. Lorenzo Capineri, University of Florence, Italy** **Prof. Riccarda Antiochia, University of Rome "La Sapienza", Italy**		
14:00 - 14:30	Wearable electrochemical microneedles-based sensors and biosensors for minimally-invasive and continuous monitoring of interstitial fluid biomarkers. **R. Antiochia**	**Prof. Riccarda Antiochia** University of Rome "La Sapienza", **Italy**
14:30 - 14:45	Ionized Gas Defelction Gyroscope **M.C. Stewart**, X. Liu and A.M. Leung	**Mr. Matthew C. Stewart**, Simon Fraser University, **Canada**
14:45 - 15:00	Surface-Enhanced InfraRed spectroscopy for selective and sensitive detection of organophosphorus compounds **P. Fehlen**, G. Thomas, F. Gonzalez-Posada Florès, T. Taliercio and D. Spitzer	**Mr. Pierre Fehlen**, University of Strasbourg, **France**
15:00 - 15:15	SIM Card-Type Responsive Polymer-Modified Paper-Based Biosensor for the Point-of-Care Determination of Creatinine in Urine E. Tzianni, M. Trachioti, A. Lazanas, A. Florou, I. Moutsios, D. Moschovas, A. Avgeropoulos, K. Govaris, L. Panagiotidis, S. Panagiotidou and **M. Prodromidis**	**Prof. Mamas Prodromidis**, University of Ioannina, **Greece**

15:15 - 15:30	Ultra-Wideband Microstrip Patch Sensor Antenna Embedded into Bra for Comfortable Breast Cancer Microwave Imaging **A. Rangel-Trejo**, J.A. Bernardo, L. Konadu and L. Fakri-Bouchet	**Mr. Abel Rangel Trejo**, CNRS-Univ Lyon, **France**
15:30 - 15:45	New Methodology to Improve an Implantable Micro-sensor for NMR Spectroscopy **J.A. Bernardo**, A. Rangel-Trejo, A. Adewolu, L. Werling, W. Uhring, L. Hebrard, C. Gontrand and L. Fakri-Bouchet	**Mr. José Bernardo**, CNRS-Univ Lyon, **France**
15:45 - 16:00	Self-Assembling DNA Hairpins for Enzyme-Free Detection of Nucleic Acids in Point-of-Care Applications **J. W. Beard**, S. L. Hunt and B. L. Miller	**Mr. Jeffrey Beard**, University of Rochester, **USA**
16:00 - 16:30	**Afternoon Coffee Break**	
Smart Materials and Surfaces - SMS 2021 Onsite Session II		
Session's Chairs: **Prof. Riccarda Antiochia, University of Rome "La Sapienza", Italy** **Prof. Mamas Prodromidis, University of Ioannina, Greece**		
16:30 - 16:45	(Sn,Ti,Nb)xO2 Solid Solution: an Innovative Sensing Material for H2 Detection **E. Spagnoli**, A. Gaiardo, B. Fabbri, M. Valt, S. Krik, M. Ardit, G. Cruciani, M. Della Ciana, L. Vanzetti, S. Gherardi, P. Bellutti , G. Vola , C. Malagù and V. Guidi	**Ms. Elena Spagnoli**, University of Ferrara, **Italy**
16:45 - 17:00	Bioorthogonal SERS nanotags for multiplex detection of biomolecules: a versatile straightforward method towards multicolor-custom palette C. Dallari, R. Innocenti, E. Lenci, A. Trabocchi, F.S. Pavone and **C. Credi**	**Dr. Caterina Credi**, National Institute of Optics, **Italy**
17:00 - 17:15	Anisotropic iridescence and polarization patterns in a direct ink written chiral photonic polymer **J. Sol**, H. Sentjens, L. Yang, N. Grossiord, A. Schenning and M. Debije	**Mr. Jeroen Sol**, Eindhoven University of Technology, **The Netherlands**
17:15 - 17:30	Photocatalytic activity of TiO2 immobilized on Corona pre-treated polypropylene films **R. Rescigno**, O. Sacco, R. Fittipaldi, V. Venditto, V. Vaiano and C. Daniel	**Ms. Raffaella Rescigno**, University of Salerno, **Italy**
17:30 - 17:45	Co-Mn mixed oxides prepared by magnetron sputtering on stainless steel meshes as catalysts for the oxidation of volatile organic compounds **P.Topka**, K. Jirátová, R. Perekrestov, M. Dvořáková, J. Balabánová, M. Koštejn, D. Pokorná, M. Čada, Z. Hubička and F. Kovanda	**Dr. Pavel Topka,** Institute of Chemical Process Fundamentals-Prague, **Czech Republic**
17:45 - 18:00	Development of thermo-responsive polymer coatings based on thiol-isocyanate chemistry to monitor the critical overheating of electronic devices **D. Bautista-Anguís**, A. Wolfberger and S. Schlögl	**Mr. Daniel Bautista**, Polymer Competence Center Leoben, **Austria**
18:00 - 18:15	Modelling and Finite Element (FE) simulation of photomechanical organic thin films **R. Cedeno**, I. Arroyo, K. Kandil, S. Aloïse and M. Nait-Abdelaziz	**Ms. Rebeca Cedeno**, University of Lille, **France**
18:15 - 18:30	A novel crystallographic orientation-based methodology to elucidate the mechanical properties of zinc alloy coatings **M. Ahmadi**, B. J. Kooi and Y. Pei	**Mr. Masoud Ahmadi**, University of Groningen, T**he Netherlands**
18:30 - 18:45	Integration of conductive fibers over wearable electronic textiles: Application of hydrogen evolution assisted (HEA) electroplating **S.M. Rosa-Ortiz**, F. Mokhtari, A.Takshi and J. Foroughi	**Ms. Sabrina Rosa**, University of South Florida, **USA**
18:45 – 19:00	Generation of cytocompatible superhydrophobic Zr-Cu-Ag metallic glass coatings with antifouling properties for medical textiles **E. Sharifikolouei**, Z. Najmi, A. Cochis, A. Calogero Scalia, M. Aliabadi, S. Perero and L. Rimondini	**Dr. Elham Sharifikolouei**, Polytechnic University of Turin, **Italy**

NanoMed 2021 Onsite Session I

Onsite Conference Giardino A

Session's Chairs:
Prof. Miriam Colombo, University of Milano-Bicocca, Italy
Prof. Francesca Granucci, University of Milano-Bicocca, Italy
Dr. Alberto Bianco, University of Strasbourg, France

08:45 - 09:15	Stimuli-responsive hybrid nanoconstructs for efficient theranostic applications in nanomedicine **V. Cauda**	**Prof. Valentina Cauda**, Polytechnic University of Turin, **Italy**
09:15 - 09:45	Labs, Cells and Organs on Chip **A. van der Berg**	**Prof. Albert van den Berg**, University of Twente, **The Netherlands**
09:45 - 10:15	Graphene-based scaffolds towards the treatment of spinal cord injuries **P. Pereira Marques**	**Prof. Paula Pereira Marques**, University of Aveiro, **Portugal**
10:15 - 10:30	Production and characterization of dual-stimuli nanofibrous membranes **A. Gonçalves**, F. Veiga Almeida, J.P. Borges and P. I. P. Soares	**Ms. Adriana Gonçalves**, CENIMAT | i3N- Caparica, **Portugal**
10:30 - 11:00	**Morning Coffee Break**	
11:00 - 11:15	Erythrocytes based carriers for therapy and diagnostic **G. Della Pelle** and N. Kostevsek	**Mrs. Giulia Della Pelle**, Jozef Stefan Institute, **Slovenia**
11:15 - 11:30	Carbon dots for nanothermometry and in vivo stem cell imaging **K.Polakova**, S.Kalytchuk, T.Malina and R. Zboril	**Dr. Katerina Polakova**, Palacký University-Olomouc, **Czech Republic**
11:30 - 11:45	Multidrug Delivery Systems Based on Polydopamine Nanoparticles **K. Żebrowska**, E. Coy, S. Jurga, R. Mrówczyński and B. Grześkowiak	**Mrs. Klaudia Żebrowska**, Adam Mickiewicz University, Poznań, **Poland**
11:45 - 12:00	A novel theranostic agent and nanoparticle drug delivery for Boron Neutron Capture Therapy **J. Sforzi**, D. Alberti, R. Stefania, A. Lanfranco, A. Deagostino, S. Aime and S. Geninatti Crich	**Mr. Jacopo Sforzi**, University of Torino, **Italy**
12:00 - 12:15	Remote control of axon outgrowth by magnetic nanoparticles A. Falconieri, S. De Vincentiis, S. Figoli, S. Ghignoli, D. Convertino, M. Mainardi, V. Cappello, L. Marchetti, M. Costa and **V. Raffa**	**Prof. Vittoria Raffa**, University of Pisa, **Italy**
12:00 - 14:00	**Lunch Break**	

Session's Chairs:
Prof. Valentina Cauda, Polytechnic University of Turin, Italy
Prof. Albert van den Berg, University of Twente, The Netherlands

14:00 - 14:30	Cutting-edge biofunctionalized nanoparticles: a step toward technological innovation **M. Colombo**	**Prof. Miriam Colombo**, University of Milano-Bicocca, **Italy**
14:30 - 15:00	Anti-inflammatory role of nanodrugs targeting the NFAT pathway in innate myeloid cells **F. Granucci**	**Prof. Francesca Granucci**, University of Milano-Bicocca, **Italy**
15:00 - 15:15	The role of colloidal stabilization and pH evolution in mesoporous silica nanoparticles formation: a comprehensive mechanistic study **V. Semeykina** and I. Zharov	**Dr. Viktoriya Semeykina**, University of Utah, **USA**
15:15 - 15:30	Covalent Chitosan-Polyethylenimine Derivatives as Gene Delivery Vehicles **L. Nicolle**, C.M.A. Journot, P. Robin, J. Casper, P. Detampel, M. Williman, H.-M. Grisch-Chan, T. Einfalt, B. Thöny, J. Huwyler and S. Gerber-Lemaire	**Ms. Laura Nicolle**, Ecole Polytechnique Fédérale de Lausanne, Lausanne, **Switzerland**
15:30 - 15:45	Novel hybrid nanoparticles for Alzheimer's disease theranostic: efficient overcoming of nanomaterials across the blood-brain-barrier **C. I. P. Chaparro**, V. Neves, J.P. Borges and P. I. P. Soares	**Ms. Catarina Chaparro**, Nova University of Lisbon, **Portugal**

15:45 - 16:00	Modulation of lipid metabolism in brain cells using poly-ion complex micelles containing CoA-conjugated CPT1A inhibitors **W. Paraiso**, J. Garcia-Chica, X. Ariza, S. Zagmutt, S. Fukushima, J. Garcia, Y. Mochida, D. Serra, L. Herrero, H. Kinoh, N. Casals, K. Kataoka, R. Rodríguez-Rodríguez and S. Quader	**Dr. West Paraiso**, Innovation Center of Nanomedicine, **Japan**
16:00 - 16:30	**Afternoon Coffee Break**	
Session's Chairs: **Prof. Albert van den Berg, University of Twente, The Netherlands** **Prof. Paula Pereira Marques, University of Aveiro, Portugal**		
16:30 - 16:45	Development of hybrid carbon nanotubes/gold nanostars for cancer treatment by hyperthermia **R. Soltani**, A. Abou-Hassan, C. Wilhelm, A. Bianco and C. Ménard-Moyon	**Ms. Rym Soltani**, University of Strasbourg, **France**
16:45 - 17:00	Flavin Adenine Dinucleotide (FAD)-Complex Gold Nanoparticles: Chemical Design, Physico-Chemical and assessment therapeutic Effects of FAD on a Breast Cancer Model of Mouse **C. Arib**, H. Liu, Q. Liu, A-M. Cieutat, D. Paleni, X. Li and J. Spadavecchia	**Ms. Arib Celia**, University of Sorbonne Paris Nord, **France**
17:00 - 17:15	Development of smart core/shell NPs as a drug platform for their further use in cancer therapy **D. Louaguef**, E. Gaffet and H. Alem-Marchand	**Ms. Dounia Louaguef,** CNRS- Lorraine University, **France**
17:15 - 17:30	Development of an effective tumor-targeted contrast agent for Mag-netic Resonance Imaging based on Mn/H-Ferritin nanocomplexes **L. Salvioni**, C.Tullio, M. Bellini, A. Degrassi, L. Fiandra, M. D'Arienzo, F. Testa, D. Prosperi and M. Colombo	**Dr. Lucia Salvioni**, University of Milano-Bicocca, **Italy**
17:30 - 17:45	Nanopore Sensing of Single-Biomolecule: Challenges in Protein Sequencing using Solid-State Nanopores **A. Nicolaï**, A. Urquiola Hernàndez and P. Senet	**Dr. Adrien Nicolaï**, CNRS-University of Bourgogne Franche-Comté, **France**
17:45 - 18 :00	A biophotonics-based biosensor for extracellular vesicles characterization in Alzheimer's disease patients **S. Picciolini**, A. Gualerzi, F. Rodà and M.Bedoni	**Dr. Silvia Picciolini**, Don Carlo Gnocchi Foundation, **Italy**
18:00 - 18:15	Biophotonics-based characterization of multifunctionalized liposomes as therapeutic agents for Glioblastoma and Alzheimer's Disease **F. Rodà**, S. Picciolini, A. Gualerzi, F. Re, A. Antoniou, S. Giofré, P. Seneci and M. Bedoni	**Mrs. Francesca Rodà**, Don Carlo Gnocchi Foundation, **Italy**
18:15 - 18:30	Development of DOTAREM-Gold-Complex: A new multifunctional nanotheranostic agent for Cholangiocarcinoma **M. Khan**, N. Djaker and J. Spadavecchia,	**Ms. Memona Khan**, University of Sorbonne Paris Nord, **France**
18:30 - 18:45	Magnetic nanoparticles to stimulate nerve regeneration on a neuroepithelial stem cell model **S. De Vincentiis**, M. Baggiani, J. Lopane, V. Cappello, M. Mainardi, M. Di Caprio, A. Falconieri, M. Costa, M. Onorati, V. Raffa	**Mrs. Sara De Vincentiis**, University of Pisa, **Italy**
18:45 – 19:00	Toxicity of carbon nanomaterials - towards reliable viability assessment via new approach in flow cytometry **T. Malina**, K. Poláková , C. Hirsch, L. Svoboda and R. Zbořil	**Mr. Tomas Malina**, Palacky University, **Czech Republic**

22 October 2021

EGF 2021 Onsite Session I		
Onsite Conference Colonne A+B		
Session's Chairs: **Prof. Vito Di Noto, University of Padova, Italy** **Dr. Eugene Kogan, Bar Ilan University, Israel** **Dr. Alberto Bianco, University of Strasbourg, France** **Prof. Paola Barbara, Georgetown University, USA**		
08:30 – 08:45	Graphene Oxide and Derivatives, Properties and Applications **B. Gjoka** and R. Wendelbo	**Dr. Blerina Gjoka**, Abalonyx As, **Norway**
08:45 - 09:00	Liquid-Phase Exfoliation of Graphene: Comparison of Laser-Induced Graphene and Graphite as Precursors **B. Kulyk**, A. F. Carvalho, D. Santos, B. F. R. Silva, A. J. S. Fernandes, B. R. Figueiredo, R. P. Silva, V. E. Abrantes, A. Bernardes and F. M. Costa	**Mr. Bohdan Kulyk**, Univ. of Aveiro, **Portugal**
09:00 - 09:15	Steam reforming towards freestanding gas phase few layer graphene **P. Fortugno**, H. Wiggers and C.Schulz	**Mr. Paolo Fortugno**, University of Duisburg-Essen, **Germany**
09:15 - 09:30	Solution Processed Graphene-Nanographene van der Waals Hetero-structures for Photodetectors with Efficient and Ultralong Charge Separation **Z. Liu**, S. Fu, A. Narita, A. Ciesielski, M. Bonn, K. Müllen, H.I. Wang and P. Samorì	**Dr. Zhaoyang Liu**, University of Strasbourg, **France**
09:30 - 09:45	Visible-frequency plasmons in nanocorrugated graphene **P. Vancsó**, G. Dobrik, P. Nemes-Incze, B. Majerus, P. Süle, G. Piszter, M. Menyhárd, B. Kalas, P. Petrik, L.Henrard and L. Tapasztó	**Dr. Peter Vancso**, Institute of Technical Physics and Materials Science, Centre for Energy Research-Budapest, **Hungary**
09:45 - 10:00	2D layered metal phosphorous trichalcogenides for electrochemical energy conversion reactions **R. Gusmao**	**Dr. Rui Gusmao**, Univ. of Chemistry and Technology Prague, **Czech Republic**
10:00 - 10:30	**Morning Coffee Break**	
10:30 - 11:00	Biodegradability and safety of carbon and bi-dimensional nanomaterials **A. Bianco**	**Dr. Alberto Bianco**, University of Strasbourg, **France**
11:00 - 11:30	Low Pt loading Hierarchical Oxygen Reduction Electrocatalysts with a Graphene "Core" and a Carbon Nitride "Shell" **V. Di Noto**, E. Negro, A. Nale, K. Vezzù and G. Pagot	**Prof. Vito Di Noto**, University of Padova, **Italy**
11:30 - 12:00	Symmetry of Electron Bands in Graphene: (Nearly) Free Electron Versus Tight-Binding **E. Kogan** and V. M. Silkin	**Dr. Eugene Kogan**, Bar Ilan University, **Israel**
12:00 - 12:15	Screening properties of graphene and its effect on electronic states **V. M. Silkin**, E. Kogan and G. Gumbs	**Prof. Vyacheslav Silkin**, Univ. of the Basque Country, **Spain**
12:15 - 12:30	Electron Diffraction and Photoemission from Few-Layer Graphene **E. Krasovskii**	**Prof. Eugene Krasovskii**, University of the Basque Country, **Spain**
12:30 - 12:45	Graphene Quantum Dots Bolometers for Studies of Single Molecule Magnets L. St Marie, L. Havlicek, J. Hruby, A. Alqahtani, D. Henry, A. Sojka, J. Navarro, R. Myers-Ward, D. Gaskill, A. El Fatimy, A. Liu, I. Nemec, P. Neugebauer and **P. Barbara**	**Prof. Paola Barbara**, Georgetown University, **USA**
12:45 - 13:00	Electrochemical Remediation of Chlorinated Ethenes Contamination Using N-functionalized Graphene Electrode **H. Ma** and H.C.B. Hansen	**Ms. Hui Ma**, University of Copenhagen, **Denmark**
13:00 - 13:15	Anaerobic Bioreduction of Dye Molecules by Ceramic-Supported Graphene Oxide Membranes **M. S. A. Amin**, F. Stüber, J. Giralt, A. Fabregat and J. Font	**Mr. Mohammad Shaiful Amin**, Rovira i Virgili University, **Spain**

13:15 - 13:30	Performance Evaluation of Nitrogen-doped Graphene / Carbon Black Supported Pt3Co Nanoparticles as PEM Fuel Cell Cathode Electrocat-alyst **D. K. Perivoliotis**, X. Jia and T. Wågberg	**Dr. Dimitrios Perivoliotis**, Umea University, **Sweden**

Virtual Presentations Sessions

The virtual presentations are to be held through the Whova Virtual event solution and can be joined online.

Any onsite participant wishing to take part of these virtual sessions, will have the room Giardino A+B available for seating.

20 October 2021

EGF 2021 Virtual Session		
Virtual Conference Room 1		
Session's Chairs: **Prof. Gerd Bacher, University of Duisburg-Essen, Germany** **Prof. Vladimir Falko, Manchester University, UK**		
10:30 - 11:00	Graphene Origami Enabled Negative Poisson's Ratio in Metal Nanocomposites **J. Yang**	**Prof. Jie Yang**, RMIT University, **Australia**
11:00 - 11:30	Mass Production Technology of CVD Graphene Materials for Setting the Cornerstone of Graphene Industry **Z. Liu**	**Prof. Zhongfan Liu**, Peking University, **China**
11:30 - 12:00	Ensuring Robust International Graphene Standards for Industry **A.Pollard**	**Dr. Andrew J. Pollard**, National Physical Laboratory, **UK**
12:00 - 12:30	Graphene in 200mm pilot line **M. Lukosius**	**Dr. Mindaugas Lukosius**, IHP, **Germany**
12:30 - 13:00	Quantum Field Theory in Graphene: a Numerical Approach **A. Rodi**	**Prof. Aleksandr Rodin**, National University of Singapore, **Singapore**
13:00 - 14:00	**Lunch Break**	
Session's Chairs: **Dr. Mindaugas Lukosius, IHP, Germany** **Dr Andrew J. Pollard, National Physical Laboratory, UK** **Prof. M. Natalia D.S. Cordeiro, University of Porto, Portugal**		
14:00 - 14:30	Ferroelectric domains and networks of piezoelectric domains in twistronic bilayers of transition metal dichalcogenides **V. Falko**	**Prof. Vladimir Falko**, Manchester University, **UK**
14:30 - 15:00	Scalable 2D materials for optoelectronic applications: Fabrication and device integration **G. Bacher**	**Prof. Gerd Bacher**, University of Duisburg-Essen, **Germany**
15:00 - 15:30	Boosting the properties of 2D materials with molecules: multi-responsive and high-performance based opto-electronic devices **P. Samori**	**Prof. Paolo Samorì**, University of Strasbourg, **France**
15:30 - 16:00	Beyond Graphene – How MXenes Expand the Range of 2D Materials for Electronics, Optics and Communication **Y. Gogosti**	**Prof. Yury Gogotsi**, Drexel University, **USA**
16:00 - 16:30	**Afternoon Coffee Break**	
Session's Chairs: **Dr. Mindaugas Lukosius, IHP, Germany** **Dr Andrew J. Pollard, National Physical Laboratory, UK**		
16:30 - 17:00	Spintronics in 2D van der waals materials **B. van Wees**	**Prof. Bart van Wees**, University of Groningen, **Netherlands**
17:00 - 17:15	Disclosing the Covalent Functionalisation of Graphene by PAMAM Dendrimers and their Applications by Molecular Simulations **M. N. D. S. Cordeiro**, V. Velachi, M. Gosika and P. K. Maiti	**Prof. M. Natalia D.S. Cordeiro**, University of Porto, **Portugal**
17:15 - 17:30	Laser Induced Backwards Transfer (LIBT) of graphene onto glass. **M. Praeger**, R. W. Eason and B. Mills	**Dr. Matthew Praeger**, Univ. of Southampton, **UK**
17:30 - 17:45	Transfer of large−area wrinkled graphene onto polymeric substrates **P. Narute**, R.S. Sharbidre, C. Jun Lee, B. Cheon Park, H-J. Jung, J-H. Kim and S-G. Hong	**Mr. Prashant Narute**, University of Science and Technology - Daejeon, **Rep. of Korea.**

17:45 - 18:00	Chemical-Free Acoustomicrofluidic Synthesis of Ultrathin Pristine Ti3C2Tz MXene Nanosheets and Quantum Dots **H. Alijani**, A. R. Rezk, M. M. Khosravi Farsani, H. Ahmed, J. Halim, P. Reineck, B. J. Murdoch, A. El-Ghazaly, J. Rosen and L. Y. Yeo	**Mr. Hossein Alijani**, RMIT University- Melbourne, **Australia**
18:00 - 18:15	Laser Induced Forward Transfer of Graphene for flexible touch sensors **A. Logotheti**, F. Zacharatos, S. Papazoglou, A. Pesquera, A. Zurutuza and I. Zergioti	**Ms. Adamantia Logotheti**, National Technical University of Athens, **Greece**
18:15 - 18:30	Memristive Graphene/Ionic Liquid Devices: Characterization and Demonstration of Associative Learning **I. Köymen**, S. Liu, S. Ergöktaş and C. Kocabaş	**Dr. Itir Koymen**, Engineering, TOBB University of Economics and Technology,**Turkey**
18:30 - 18:45	Dirac nodal- loops in two-dimensional Cu2Si **M. Cameau**, C.-H. Chen, A. Huang, R. Ishibiki, T. Kondo, H.-T. Jeng, I. Matsuda and M. D'angelo	**Mr. Mathis Cameau**, Sorbonne University, **France**
18:45 - 19:00	Graphene-coated E-textiles based on hydrophilic and hydrophobic fabrics **B. Meskini**, T. Bashir and N-K. Persson	**Mr. Bilel Meskini**, University of Borås, **Sweden**
19:00 - 19:15	Fabrication of Graphene/n-Silicon Schottky Heterojunction for Detection of Free Chlorine in Aqueous Solutions **S. Angizi**, P. Ravi Selvaganapathy and P. Kruse	**Mr. Shayan Angizi**, McMaster University, **Canada**

21 October 2021

Smart Materials and Surfaces - SMS 2021 Virtual Session		
Virtual Conference Room 1		
Workshop on InComEss EU Project: **INnovative polymer-based COmposite systeMs for high-efficient Energy Scavenging and Storage**		
Session's Chairs: **Dr. Cintia Mateo-Mateo, AIMEN, Spain**		
08:00 - 08:15	InComEss project overview **C. Mateo-Mateo**	**Dr. Cintia Mateo-Mateo**, AIMEN, **Spain**
08:15 - 08:45	Graphene liquid crystal-based dielectrics **P. Poulin**	**Dr. Philippe Poulin**,Centre de Recherche Paul Pascal-CNRS- Bordeaux, **France**
08:45 - 09:15	Li-ion batteries: characterization using EIS **R. Novoa**	**Dr. X. Ramón Novoa**, University of Vigo, **Spain**
09:15 - 09:30	Development of lead-free piezoelectric fibres **N. Azoia**	**Dr. Nuno G. Azoia**, CeNTI, **Portugal**
09:30 - 09:45	Research on thermoelectric polymer-based composites at IPF Dresden **B. Krause**	**Dr. Beate Krause**, Leibniz Institute for Polymer Research, **Germany**
09:45 - 10:00	Printed monolithic supercapacitor **M. Mäntysalo**	**Prof. Matti Mäntysalo,** Tampere Univ., **Finland**
10:00 - 10:15	Piezoelectric Vibration Energy Harvester – State of the Art Systems Implementations and Economics **J. Kunzmann**	**Dr. Jan Kunzmann** & **Enrique de Pablo Corona** Smart Materials GMBH**, Germany**
10:15 - 10:30	Development of High Energy Ultracapacitors from an Industrial Perspective **M. Klose**	**Mr. Markus Klose**, Skeleton Technolologies, **Estonia**
10:30 - 11:00	**Morning Coffee Break**	
Session's Chairs: **Prof. Nuria Aliaga-Alcalde, ICMAB-CSIC Barcelona, Spain** **Prof. Aimé Lay-Ekuakille, University of Salento, Italy**		
11:00 - 11:30	Molecular Switches at Interfaces and in Junctions: A Theoretical Insight **J. Cornil**	**Prof. Jérôme Cornil**, Université de Mons, **Belgium**
11:30 - 12:00	Micatronics: A New Platform for Soft Transparent Technology **Y-H Chu**	**Prof. Ying-Hao Chu**, National Tsing-Hua Univ., **Taiwan**
12:00 - 13:00	**Lunch Break**	
Session's Chairs: **Prof. Jérôme Cornil, Université de Mons, Belgium** **Dr. Anna Laromaine, Institut Ciencia de Materials de Barcelona, Spain** **Prof. Aimé Lay-Ekuakille, University of Salento, Italy**		
13:00 - 13:15	Laser based pick and place of 2D nanomaterials **N.T. Goodfriend**, O. Gatsa, A.V. Bulgakov, O. A. Nerushev, T. Hotta, C. Zhao, R. Kitaura, E.E.B. Campbell, N.M. Bulgakova and T. Mocek	**Dr. Nathan Goodfriend**, HiLASE Centre, Inst. of Physics of the Czech Academy of Sciences, **Czech Republic**
13:15 - 13:30	Extending the scope for Curcuminoids: from active components on graphene devices to the creation of 2D materials **N. Aliaga-Alcalde**, A. González-Campo, D. Herrera-Miranda, R. Zaffino, D. Riba-López, T. Carcona-Lamarca, R. Díaz-Torres, L. Rodríguez-Cid, C. Domingo, M. Soler, H. van der Zant and E. Ruiz	**Prof. Nuria Aliaga-Alcalde**, ICMAB-CSIC Barcelona, **Spain**
13:30 - 13:45	Curcuminoid-based active surfaces towards the development of new metal heterogeneous detectors **A. González-Campo**, R. Gimeno-Múñoz and N. Aliaga-Alcalde	**Dr. Arantzazu Gonzalez-Campo**, ICMAB-CSIC-Barcelona, **Spain**

13:45 - 14:15	Smart Electromagnetic Surfaces: A Key-Enabling Technology for Future Wireless Systems M. Barbuto , Z. Hamzavi-Zarghani, M. Longhi, A. Monti, D. Ramaccia, S. Vellucci, A. Toscano and **F. Bilotti**	**Prof. Filiberto Bilotti**, Roma Tre University, **Italy**
14:15 - 14:45	Emerging Applications of Boron Nitride Nanotubes for Advanced Electronics and Biomedicine **Y. Khin Yap**	**Prof. Yoke Khin Yap**, Michigan Technological University, **USA**
14:45 - 15:00	Rational Design of RbIxMnII[FeIII(CN)6](2+x)/3.zH2O (RbMnFe) Prussian Blue Analogue (PBA) Nanoparticles (NPs) for Switchable Magnetic and Non-linear Optical Properties **T. T. Vu**, N. Daro, S. Mornet, E. Freysz and G. Chastanet	**Ms. Thi Thiet Vu**, University of Bordeaux, **France**
15:00 - 15:15	Transport of Magnetic Microparticles on a Self-Assembled 2D Lattice through an Externally Monitored Potential **F. Martínez-Pedrero**, F. Ortega, R.G. Rubio and C. Calero	**Dr. Fernando Martínez-Pedrero**, Complutense University of Madrid, **Spain.**
15:15 - 15:30	Challenges on fabrication of the microstructured magnetic actuation systems based on Ni-Mn-Ga single crystal **D. Musiienko**, M. Kohl and O. Heczko	**Dr. Denys Musiienko**, Institute of Physics of the Czech Academy of Sciences, **Czech Republic**
15:30 - 16:00	**Afternoon Coffee Break**	
Session's Chairs: **Prof. Yoke Khin Yap, Michigan Technological University, USA** **Dr. Petr Sittner, Czech Academy of Sciences, Czech Republic**		
16:00 - 16:15	Biomimetic fiber webs based on conducting polymer with actuation and self-sensing capabilities **M. Beregoi**, A. Evanghelidis and I. Enculescu	**Dr. Mihaela Beregoi**, National Institute of Materials Physics, **Romania**
16:15 - 16:30	Shaped organic printed films for photosensing devices **S. Sequeira**, V. C. Martins, R. Vilarinho, J. Agostinho Moreira, S. Cardoso, H. Alves and D. C. Leitao	**Ms. Sara Sequeira**, INESC-MN-Lisbon, **Portugal**
16:30 - 17:00	Catalytic transformation of methane to C1-C2 **J. Tang**	**Prof. Junwang (John) Tang**, University College London, **UK**
17:00 - 17:30	Material Computations for Energy Storage **W. Lu**	**Prof. Wei Lu**, University of Michigan, **USA**
17:30 - 17:45	Novel platinum (II) complexes for light-emitting devices **F. Fagnani** , A. Colombo, C. Dragonetti, D. Roberto, D. Marinotto and M. Cocchi	**Mr. Francesco Fagnani**, University of Milan, **Italy**
17:45 - 18:00	Pixelated Smart Window for High Dynamic Range Signage Displaying Applications **Q. Jin**, Q. Zhang, J. Chen, T. Gehring, S. Eizaguirre, R. Huber, G. Gomard, U. Lemmer and R. Kling	**Mr. Qihao Jin**, Karlsruhe Institute of Technology, **Germany**
18:00 - 18:15	Telomeric DNA Fragments and Carbon Nanotubes as pH Controlled Carriers of Doxorubicin. Molecular Level Analysis. **T. Panczyk**	**Prof. Tomasz Panczyk**, Jerzy Haber Institute of Catalysis and Surface Chemistry, **Poland**
18:15 - 18:30	Ionic Liquids as a green tool for melanin manipulation at the nanoscale: nanotechnological perspectives **M. Ambrico**, P. Manini, L. Guazzelli, A. Mezzetta, L. Valgimigli, P.F. Ambrico, T. Ligonzo and M. d'Ischia	**Mrs. Marianna Ambrico**, CNR– ISTP- Bari, **Italy**
18:30 - 18:45	Innovative virtual approach for treatment of fears and enhancement of cognitive abilities G.Scavone, D.Benatti, M.Donadio, A.Ruoto, D. Sinitò, E. Massa and **V. Santarcangelo**	**Dr. Vito Santarcangelo**, iInformatica Srl, **Italy**

22 October 2021

Sensors 2021 Virtual Session		
Virtual Conference Room 1		
Session's Chairs: Session's Chairs: **Prof. Danila Moscone, University of Rome Tor Vergata, Italy** **Prof. Carole Chaix, Claude Bernard University Lyon 1, France** **Dr. Stela Maria Pruneanu, INCDTIM Cluj-Napoca, Romania**		
08:30 - 09:00	Applications of Graphene Modified Electrodes **S.M. Pruneanu**	**Dr. Stela Maria Pruneanu**, INCDTIM Cluj-Napoca, **Romania**
09:00 - 09:15	Validation of data from an artificial sniffer dog by common analytical techniques. **I. Hardy**, M. H. Jakobsen, T. Treiberg, C. H. Gotfredsen and E. Dossi	**Ms. Iona Hardy**, Cranfield University, **UK**
09:15 - 09:30	pH sensor using silver nanoparticles embedded in silica-coated optical fibres **S. Debnath**, Y-C. Chen, T. Green, G. Hinds and S. Roy	**Mr. Shaon Debnath**, University of Strathclyde, **UK**
09:30 - 09:45	Rapid, Cost-Effective, and Intelligible Bi-Electrode Electrochemical Sensing System for Detection of Attomole-Level Dengue Virus Sequence **T. Agarkar**, S. Ghosh and A. Kumar	**Ms. Tanvi Agarkar**, Bennett University, **India**
09:45 - 10:00	Widening the Range of Trackable Environmental and Health Pollutants for Li-Garnet-Based Sensors **M. Balaish** and J. L.M. Rupp	**Dr. Moran Balaish**, Massachusetts Institute of Technology, **USA**
10:00 - 10:30	**Morning Coffee Break**	
10:30 - 10:45	New illumination / sensing platform **R. Trihan**, A. Aimable, F. Rossignol, J. Kowalko, H. Węglarz, A. Szysiak, A. Kozłowska, B. Fetliński, B. Janaszek, M. Kaczkan, M. Ihle, S. Ziesche, P. Giemza and M. Szczypa	**Dr. Romain Trihan**, Institute of Research for Ceramics- Limoges, **France**
10:45 - 11:00	BTEX Detection: Merging MEMS Technology with Metal Ion-Functionalized Au MPCs to Exploit Cation-π Interactions **P. K. Adhihetty**, S. Halder, D. M. Smith, X. Fu and M. H. Nantz	**Mrs. Prasadanie Adhihetty**, University of Louisville, **USA**
11:00 - 11:15	Effect of scattering loss on optimized waveguide enhanced Raman spectroscopy sensors **Z. Liu**, M.A. Ettabib, J.S. Wilkinson and M.N. Zervas	**Mr. Zhen Liu**, University of Southampton, **UK**
11:15 - 11:45	Paper-based electrochemical (bio)sensors as novel more sustainable devices **D. Moscone**	**Prof. Danila Moscone**, University of Rome Tor Vergata, **Italy**
11:45 - 12:00	Bioanalytical Applications of Enzyme-Mimicking Inorganic Nanoparticles **V.G. Panferov**, I.V. Safenkova, N. A. Byzova, A.V. Zherdev, B.B. Dzantiev and A.N Bach	**Dr. Vasily Panferov**, Research Center of Biotechnology of the Russian Academy of Sciences, **Russia**
12:00 - 12:15	Quartz crystal microbalance-based sensor for accurate quantification and administration of drug loaded solid lipid nanoparticles for drug re-lease in-vitro study **M. Consumi**, L. Talarico, G. Leone and A. Magnani	**Dr. Marco Consumi**, University of Siena, **Italy**
12:15 - 12:30	Sensing in Service of Cultural Heritage Protection from Negative Effects of Climate Change **A. Krukowski** and E. Vogiatzaki	**Dr. Artur Krukowski**, RFSAT-Limited, **Ireland**
12:30 – 12:45	Highly fluorescent organic radical nanoparticles as nanothermometer for biological applications **N. Gonzalez-Pato**, D. Blasi, I. Diez-Zabala, S. Srinivasan, X. Rodriguez-Rodriguez, J. Guasch, A. Laromaine, J. Veciana and I. Ratera	**Ms. Nerea González Pato,** Institute of Material Science of Barcelona (ICMAB-CSIC), **Spain.**
12:45 – 13:00	Real-time Thermographic Object Tracking of the Body Temperature of a Neonate **K. Rassels** and P.J. French	**Mr. Kianoush Rassels**, TU-Delft, **The Netherlands**

22 October 2021

NanoMed 2021 Virtual Session

Virtual Conference Room 2

Session's Chairs:
Prof. Nuno C. Santos, iMM Lisbon, Portugal
Dr. Gerard Tobias, ICMAB-CSIC, Spain

08:30 - 09:00	Gold Nanorods as Theranostic Agent. Applications in Barret Oesophagus, Hepatocarcinoma and Bladder Cancer **M. Comes Franchini**	**Dr. Mauro Comes Franchini**, University of Bologna, **Italy**
09:00 - 09:30	Atomic force microscopy as a nanotool for the assessment of cardiovascular patients **N.C. Santos**	**Prof. Nuno C. Santos**, iMM Lisbon, **Portugal**
09:30 - 09:45	AgNP synthesized by reduction with natural photosensitizer hypericin **R. Rey-Méndez**, N. González-Ballesteros, F. Fabbri, G. Salviati, F. Bigi and M.C. Rodríguez-Argüelles	**Ms. Raquel Rey-Mendez**, University of Vigo, **Spain**
09:45 - 10:00	Deformable liposomes loaded into dissolving microneedle array for metastatic melanoma targeting: a preformulation study. **S. Demartis**, AJ. Paredes, F. Volpe-Zanutto, LK. Vora, E. Lupinu, E. Gavini and RF. Donnelly	**Ms. Sara Demartis**, University of Sassari, **Italy**
10:00 - 10:15	Ultra-Magnetic Liposomes: a Versatile Tool for Cancer Therapy C. Thebault, A. Michel, J. Seguin, N. Mignet, B.-T Doan and **C. Ménager**	**Prof. Christine Ménager**, Sorbonne University, **France**
10:00 - 10:30	**Morning Coffee Break**	
10:30 - 11:00	RNA gene medicines: evolution of synthetic carriers **E. Wagner**	**Prof. Ernst Wagner**, Ludwig-Maximilians Univ, **Germany**
11:00 - 11:30	Hybrid nanomaterials for biomedical imaging **G. Tobias**	**Dr. Gerard Tobias**, ICMAB-CSIC, **Spain**
11:30 - 12:00	Quantum water" in nanoparticulate systems which has a great influence on membrane penetration **I.T. Degim**	**Prof. Ismail Tuncer Degim**, Biruni University-Istanbul, **Turkey**
12:00 - 12:15	Temperature-responsive nanogels containing SPIONs and miRNAs for targeted delivery in wound healing and skin regeneration applications. The EuroNanoMed project TENTACLES A. Paolini, S.P. Bruno, A. Sobolevs, A. Plotniece, M.K. Chmielewski, N. Krówczyńska, L. Le Hégarat, K. Hogeveen, M. Sramkova, A. Gabelova, A. Caporali, N. Cassinelli, B. Sanz and **A. Masotti**	**Dr. Andrea Masotti**, Bambino Gesù Children's Hospital-IRCCS, **Italy**.
12:15 - 12:30	Antimicrobial Nanomaterials: will be able to generate Bacterial Resistance? **B.L. España-Sánchez,** F.B. Ramírez Montiel, N.A. Hernández-Santos, M.M. Hernández-Orozco, F. Padilla-Vaca, M.Y. Reyes-Vidal and G. Luna-Bárcenas	**Dr. Beatriz Liliana España Sánchez**, Center of Research and Technology Development in Electrochemistry, **Mexico**
12:30 - 12:45	Nanosystems as enhancements of cell regeneration **A. Minò**, G. Testa and L. Ambrosone	**Mr. Antonio Minò**, Univeristy of Molise, **Italy**
12:45 - 13:00	Molecular Dynamic study of antitumoral drug Cisplatin confinement inside edge-functionalized carbon nanotubes and its release near cell membrane **A. Mejri**, B. Tangour, G. Herlem and F. Picaud	**Dr. Alia Mejri**, Université Bourgogne Franche-Comte, **France**
13:00 - 13:15	Evaluation of cytotoxicity of thiolated organosilica nanoparticles and the effect of PEGylation on toxicity reduction **B. A. Zhaisanbayeva**, E. A. Mun, I.A. Vorobjev, G. Hortelano and V. V. Khutoryanskiy	**Ms. Balnur Zhaisanbayeva**, Nazarbayev University, **Kazakhstan**

Posters Session

As the event is held on hybrid mode, all Posters are being displayed through the Whova solution

N.	Poster Title	Author, Affiliation, Country
1.	Liquid/aerosol-based atmospheric pressure plasma deposition (APPD) of nanoparticle and metal salt-containing HMDSO coatings **E. Pycha**, S. Chwatal, M. Stummer, S. Gümüs, A. Schwan, J. Lackner and W. Waldhauser	**Ms. Eva Pycha**, Joanneum Research, **Austria**
2.	Laser texturing of PET in silver nanoparticle colloids **J. Siegel**, J. Pryjmaková and V. Švorčík	**Dr. Jakub Siegel**, Univ. of Chemistry and Technology Prague, **Czech Rep.**
3.	Cellulose-based composite aerogel: perspectives for environmental applications **M. Zannotti**, A. Rossi and R. Giovannetti	**Dr. Marco Zannotti**, University of Camerino, **Italy**
4.	High Sensitive Ultrathin Flexible Thermoplastic Polyurethane/Carbon Black Fibrous Film Strain Sensor with Adjustable Scaffold Networks **X. Wang**, X. Liu, and D. W. Schubert	**Mr. Xin Wang**, Friedrich-Alexander-University Erlangen-Nuremberg, **Germany**
5.	Fast and Green Fabrication of Silica Nanoparticles Coated with Nanosilver as Efficient Antimicrobial Agents **A. Abduraimova**, T. Mulikova, A. Duisembekova, A. Molkenova, D. Kanayeva and T.S. Atabaev	**Ms. Aiganym Abduraimova**, Nazarbayev University, **Kazakhstan**
6.	Influence of different types of modifiers on ice adhesion and hydrophobic properties of epoxy resins **G. Morgiante**, M. Piłkowski and J. Marczak	**Dr. Gianluca Morgiante**, Polish Center for Technology Development- Wrocław, **Poland**
7.	Optimization of the Optical Characteristics of a Multilayer Coating with Thin Films of Germanium Telluride **E. Pritotskii** and M. Pankov	**Mr. Egor Pritotskii**, Institute on Laser and Information Technologies of Russian Academy of Sciences, **Russia**
8.	Fluorinated compound as surface free energy lowering agent in hydrophobic coatings **M. Piłkowski**, G. Morgiante and J. Marczak	**Mr. Michał Piłkowski**, Polish Center for Technology Development- Wrocław, **Poland**
9.	Surface Coatings for Small Aircraft Brakes Application **M. Granata** and F. Bellucci	**Dr. Marco Granata**, CRdC Tecnologie Scarl, **Italy**
10.	Characterization of materials resulted form spent automotive catalysts using spectrometric techniques **M. Senila**, O. Cadar, S. Böringer, K. Seaudeau-Pirouley and P. Lacroix-Desmazes	**Dr. Senila Marin**, INCDO-INOE 2000, Research Institute for Analytical Instrumentation, **Romania**
11.	Bipolar Benzophenone Compounds Bearing Tetrahydrocarbazolyl- and 2-Phenylindolyl- moieties for Application in Optoelectronics **E. Jatautiene**, R. Keruckiene, J. Keruckas, R. Sebastine Bernard, J. Simokaitiene, D. Volyniuk and J. Vidas Grazulevicius	**Dr. Egle Jatautiene**, Kaunas University of Technology, **Lithuania**
12.	Mechanochromic luminescent properties of donor-acceptor type organic emitters based on benzanthrone and carbazole moities **D. Volyniuk**, U.Tsiko, G. Sych, O. Bezvikonnyi, R. Keruckiene, J. Keruckas, R. Sebastine Bernard, E. Jatautiene, A. Lazauskas and J. Vidas Grazulevicius	**Dr. Dmytro Volyniuk**, Kaunas University of Technology, **Lithuania**
13.	Amplification of Pyroelectric Device with WSe2 Field Effect Transistor and Ferroelectric Gating **S. Mbisike**, J. Phair, L. Eckart and R. Cheung	**Mr. Stephen Mbisike**, University of Edinburgh, **UK**
14.	Fabrication of PVDF Porous Structure via Fused Filament Fabrication for Energy Harvesting **A. Saleh**, G.W. Melenka and S Ning Leung	**Ms. Ayatullah Elsayed**, York University, **Canada**
15.	Electrochemical detection of cymoxanil fungicide with new graphene modified glassy carbon electrode **C. Varodi**, A. Ciorita, A. Turza, F. Pogacean, M. Coros and S. Pruneanu	**Dr. Codruta Varodi**, INCDTIM Cluj-Napoca, **Romania**
16.	Molecular Dynamics of Graphene-Electrolyte Interface: Effects of Charged Graphene on Interfacial Solution Structure and Molecular Diffusion **J. Dočkal**, M. Lísal and F. Moučka	**Mr. Jan Dočkal**, J. E. Purkinje University, **Czech Republic**

17.	Synthesis of Heteroatom co-doped Graphene Nanostructures and their Applications **M Coroş**, F Pogăcean, C Varodi, A Turza, T Radu A Cioriţa and S Pruneanu	**Dr. Maria Coros**, INCDTIM Cluj-Napoca, **Romania**
18.	Electrocatalytic properties of NGr-ZnO hybrid materials **F. Pogacean**, M. Stefan, C. Varodi, M. Coros, L. Magerusan, V. Mirel and S. Pruneanu	**Dr. Florina Pogacean**, INCDTIM Cluj-Napoca, **Romania**
19.	Trifluoromethylphenyl-disubstituted derivatives of dimethylacridan and phenothiazine for multifunctional sensing and lighting applications **R. Keruckiene**, B-Y. Lin, C.-H. Chen, C.-C. Chu, C.-F. Lin, T.-L.Chiu, J.-H. Lee and J. V. Grazulevicius	**Dr. Rasa Keruckienė**, Kaunas University of Technology, **Lithuania**
20.	Multifunctional silica-based sensors for real-time viral screening **P. Robin**, C.M.A. Journot, L. Mayoraz, D. Nicolis, L. Barnebei, C. Tiarantelli, L. Cascione, F. Lucarini, D. Staedler, F. Bertoni, I. Stefanini and S. Gerber-Lemaire	**Ms. Perrine Robin**, École Polytechnique Fédérale de Lausanne, **Switzerland**
21.	Two-dimensional Pnictogens (Monoelemental Nanosheets of Bi or Sb) as Transducing Materials in Electrochemical Sensing **A. Lazanas** and M. Prodromidis	**Mr. Alexandros Lazanas**, University of Ioannina, **Greece**
22.	3D-Sparking Head Aided Screen-Printed Electrode-to-Graphite Pencil In-situ Tailoring of Sensing Surface with Graphitic Nanomaterials: Application to the Determination of Guanine and Adenine in Saliva and of 8-hydroxy-2΄-deoxyguanosine in Urine **M. Trachioti**, A. Papavasileiou, J. Hrbac and M. Prodromidis	**Ms. Maria Trachioti**, University of Ioannina, **Greece**
23.	Combining Health Coaching with Remote Monitoring: A Study of the Effectiveness for Hypertension Patients C. Markert, K. Zahed and **F. Sasangohar**	**Prof. Farzan Sasangohar**, Texas A&M University, **USA**
24.	Molecular layering method as base for producing of smart materials **N.V. Zakharova** and A.A. Malygin	**Mrs. Natalia Zakharova**, St. Petersburg State Technological Instit., **Russia**
25.	Iterative non-negative constrained deconvolution for waveguide enhanced Raman spectroscopy signal recovery **Z. Liu**, M.A. Ettabib, B.M. Bowden, A. Marti, P.N. Bartlett, J.S. Wilkinson and M.N. Zervas	**Mr. Zhen Liu**, University of Southampton, **UK**
26.	High Triplet Energy Aryl Sulfones for Exciplex-Based White Electroluminescent Devices **J. Keruckas**, X. Tan, D. Volyniuk, J.V. Gražulevičius, R.S. Bernard, U. Tsiko, K. Ivaniuk, I. Helzhynskyy and P. Stakhira	**Dr. Jonas Keruckas**, Kaunas University of Technology, **Lithuania**
27.	Disposable amperometric aptasensor for Troponin I based on carboxy-ethylsilanetriol-modified graphene oxide coated electrodes **A. Villalonga**, I. Estabiel, A. M. Pérez-Calabuig, B. Mayol, C. Parrado and R. Villalonga	**Ms. Anabel Villalonga**, Complutense University of Madrid, **Spain**
28.	Monitoring of the evolution of human chronic wounds using a ninhydrin-based sensory polymer and a smartphone **S. Vallejos**, M. Guembe-García, V. Santaolalla-García, N. Moradillo-Renuncio, S. Ibeas, J.A. Reglero, F.C. García, J. Pacheco, S. Casado and J.M. García	**Dr. Saul Vallejos**, The university of Burgos, **Spain**
29.	Impact of patch-potentials on capacitive displacement measurements **L. Daul**, I. Busch, T. Jin, L. Koenders, M. Weinert and H. Wolff	**Mr. Lars Daul**, The Physikalisch-Technische Bundesanstalt (PTB), **Germany**
30	Polymer-ceramic composites containing hydroxyapatite for supporting bone tissue regeneration **B. Tyliszczak,** M. Głąb, A. Drabczyk, S. Kudłacik-Kramarczyk and A. Sobczak-Kupiec	**Prof. Bożena Tyliszczak**, Cracow University of Technology, **Poland**
31.	Smart composites as carriers of active substances **A. Sobczak-Kupiec**, D. Słota, W. Florkiewicz, K. Piętak and M. Dyląg	**Prof. Agnieszka Sobczak-Kupiec,** Cracow University of Technology, **Poland**
32.	Polymer-ceramic composite coatings modified with active agents **W. Florkiewicz**, D. Słota, K. Piętak, B. Tyliszczak and A. Sobczak-Kupiec	**Mrs. Wioletta Florkiewicz**, Cracow University of Technology, **Poland**
33.	Biocompatibility assessment of polymer-ceramic composites loaded with plant extract **D. Słota**, W. Florkiewicz, K. Piętak, A. Szwed, M. Włodarczyk, M. Siwińska, K. Rudnicka and A. Sobczak-Kupiec	**Mrs. Dagmara Słota**, Cracow University of Technology, **Poland**

34.	Tuning the size, shape and pore structure of mesoporous silica nanoparticles **M. Llenas**, S. Sandoval, C. Martínez, M. Florensa and G. Tobias	**Ms. Marina Llenas Martínez**, ICMAB-CSIC, **Spain**
35.	Redox-Sensitive Core-Multishell Nanocarrier Systems **K. Rajes**, K. A. Walker, S. Hadam, F. Zabihi, J. Ibrahim-Bacha, G. Germer, P. Patoka, B. Wassermann, F. Rancan, E. Rühl, A. Vogt and R. Haag	**Ms. Keerthana Rajes**, The Free University of Berlin, **Germany**
36.	Functionalization of harmonic nanoparticles for multimodal imaging and theranostic applications. **A. Gheata**, R. De Matos, J. Vuilleumier, G. Gaulier, G. Campargue, L. Bonacina, D. Staedler, D. Diviani and S. Gerber-Lemaire	**Mr. Adrian Gheata**, École Polytechnique Fédérale de Lausanne, **Switzerland**
37.	Synthesis and characterization of multifunctional iron-doped ZnO nanoparticles for anti-tumoral applications **M. Carofiglio**, M. Laurenti, L. Racca, S. Barui, N. Garino and V. Cauda	**Mr. Marco Carofiglio,** The Polytechnic University of Turin, **Italy**
38.	Developing doped ZnO-based immunocompatible tumor targeted nanotheranostics to improve pancreatic cancer treatment **S. Barui**, N.M. Percivalle, M. Conte, B. Dumontel, L. Racca, M. Carofiglio and V. Cauda	**Dr. Sugata Barui**, The Polytechnic University of Turin, **Italy**
39.	Investigation of the anticancer effects of ZnO nanocrystals remotely activated **L. Racca** and V. Cauda	**Dr. Luisa Racca**, The Polytechnic University of Turin, **Italy**
40.	Protein-stabilized amorphous Titania Nanoparticles for Sonodynamic Therapy **V.Vighetto**, L. Racca, M. Canta, J.C. Matos, M. Clara Gonçalves and V. A. Cauda	**Ms. Veronica Vighetto**, The Polytechnic University of Turin, **Italy**
41.	In vitro evaluation of biomimetic nanoparticles for liver cancer treatment **M. J. Bigaj-Józefowska**, E. L. Coy, M. Grabowska, S. Jurga and B. F. Grześkowiak	**Ms. Magdalena Bigaj-Józefowska**, Adam Mickiewicz University, **Poland**
42.	Development of Multifunctional Nanocarriers Based on PAMAM Dendrimers for Gene/drug co-delivery for Targeted Colorectal Cancer Therapy **B. Bulkurcuoğlu**, MU Gurbuz, K. Pavlov, S. Tyciakova, M Matuskova, M Tulu and S Ercelen	**Mr. Bünyamin Bulkurcuoğlu**, TUBITAK MRC Genetic Engineering and Biotechnology Institute, **Turkey**
43.	Simple design of antibody-based microarrays via DNA-directed immobilization in multiplex diagnostics of viral infections **S. Karoń,** M. Drozd and E. Malinowska	**Ms. Sylwia Karoń**, Warsaw University of Technology, **Poland**
44.	Magnetically Induced Cargo Release Inside Living Cells **L.M. Nack**, Z. Li, D. Zhu and W.J. Parak	**Mr. Leroy M. Nack**, University of Hamburg, **Germany**
45.	Delivery of Macromolecular Drugs via Silica Particle Based Surface Coatings **Y. Brasse** and A. Kraegeloh	**Dr. Yannic Brasse**, Leibniz Institute for New Materials, **Germany**
46.	Stimuli-Responsive Polymer-Coated Gold Nanourchins for Controlled Delivery of Dasatinib Hydrophobic Tyrosine Kinase Inhibitor **A-S. Tatar**, M. Baia, S. Astilean and S. Boca	**Dr. Andra-Sorina Tatar**, Babeș-Bolyai University, **Romania**
47.	Gelidium corneum mediated synthesis of gold nanoparticles with enhanced antiinflamatory and antioxidant potential **N. González-Ballesteros**, L. Diego-González, M. Lastra-Valdor, M. Grimaldi, A. Cavazza, F. Bigi, R. Simón-Vázquez and M. C. Rodríguez-Argüelles	**Dr. Noelia González Ballesteros**, University of Vigo, **Spain**
48.	Enzyme-controlled Mesoporous Nanomachine for Triple-responsive Controlled Delivery **B. Mayol**, V. Dato, M. Estravís, C. de la Torre, P. Díez, S. Jimenez-Falcao, A. Villalonga, F. Sancenón, A. Sánchez, P. Martínez-Ruiz, R. Martínez-Máñez and R. Villalonga	**Ms. Beatriz Mayol**, Complutense University of Madrid, **Spain**
49.	Evaluation of green nanofibers-based composite materials as biosensor for selective glycoproteins detection **M. Florescu**, M. David, K. Mamatkulov and G. Arzumanyan	**Dr. Monica Florescu**, Transilvania University of Brasov, **Romania**
50.	Determination of glucosamine hydrochloride used for the treatment of periodontal disease by high performance liquid chromatography **D. A. Scurtu**, O. Cadar, E. Kovacs, L. Senila and C. Roman	**Dr Daniela Alexandra Scurtu**, INCDO INOE 2000, ICIA Cluj-Napoca, **Romania**
51.	Biodistribution of Gold in Mice Tissues with Gold Nanostructured Compound Administration **O. Cadar**, M. Senila, A.I. Torok and T. Mocan	**Dr. Oana Cadar**, INCDO INOE 2000, ICIA Cluj-Napoca, **Romania**

52.	Determination of Trace Amounts of Silver in Various Simulated Biological Fluids by Graphite Furnace Atomic Absorption Spectrometry **O. Cadar**, D. Scurtu, A.M. Hoaghia and A. Ilea	**Dr. Oana Cadar**, INCDO INOE 2000, ICIA Cluj-Napoca, **Romania**
53.	Development and validation of a spectrometric method for the evaluation of biodistribution of gold nanoparticles **A.I. Torok**, C. Tanaselia, T. Mocan and O. Cadar	**Dr. Anamaria Iulia Torok**, INCDO INOE 2000, ICIA Cluj-Napoca, **Romania**
54.	SiO2-decorated Parylene C micropillars designed to probe cellular force **Z. Fohlerova**, I. Gablech, A. Otahal and P. Fecko	**Dr. Zdenka Fohlerova**, Brno University of Technology, **Czech Rep**.
55.	Selective Detection of Nickel Ions with Silver Nanoparticle-Based Sensor **A. Rossi**, M. Zannotti, M. Cuccioloni, M. Minicucci, L. Petetta, M. Angeletti and R. Giovannetti	**Mr. Andrea Rossi**, University of Camerino, **Italy**
56.	Functionalized self-assembled AuNPs at the liquid-liquid inter-face with alkyne-based ferrocenyl derivative **J. Catalán-Toledo** and N. Crivillers	**Mr. Jose Catalan Toledo**, ICMAB-CSIC), **Spain**
57.	Ferrocene-containing Porous Poly(ionic liquid) Membrane and its Conversion into Porous Iron Oxide Film **A. Khorsand Kheirabad** and J. Yuan	**Ms. Atefeh Khorsand Kheirabad**, Stockholm University, **Sweden**
58.	Porous Silicon-Based Microarray Platforms with Carbon Dots Functionalization for Enhanced Viral Detection **L. Gogianu**, M.A. Popescu, A. Radoi, A. Sălceanu, A. Boldeiu, G. Craciun and M. Simion	**Ms. Larisa Gogianu**, National Institute for Research and Development in Microtechnologies – IMT Bucharest, **Romania**
59.	THEVETIA PERUVIANA ROOTS EXTRACT MEDICATED GOLD NANOPARTICLES AND ITS UREASE INHIBITORY ACTIVITY **S. Bawazeer**	**Mr. Saud Bawazeer**, Department Pharmacutical Chmistry, University Umm Al-Qura Univeristy, Makkah, **Saudi Arabia**
60.	Anthraquinone-carbon modified as hybrid electrode for energy storage system **S. Alshehri**, G. Wildgoose, J. Fielden	**Ms. Sarah Alshehri**, University of East Anglia, **UK**
61.	Radiation Curable Hydrophobic Fluorinated Palm Oil based Urethane Acrylate Resin for Wood Coating Application N.B. Ismail, A. N. Jamaluddin, N.Othman, M.S. Alias, K. A. A. Halim, M. Mohamed, R. Tajau and **M. H. Harun**	**Dr. Mohd Hamzah Harun** Radiation Processing Technology Division, Malaysian Nuclear Agency, **Malaysia**
62.	Bi-Layered Cantilever Based Opto-Mechanical Holographic Sensor **F.R. McGovern**, C. Grogan, G. Amarandei, I. Naydenova	**Mr. Faolan Radford McGovern**, Technological University Dublin, **Ireland**
63.	Development of volume holographic optical elements for application in wound healing monitoring **P. Stoeva**, T. Mikulchyk, B. Rogers, M. Oubaha, S. Martin, D. Cody, M.A. Ferrara, G. Coppola, and I. Naydenova	**Ms. Pamela Stoeva**, Technological University Dublin, **Ireland**

Smart Materials & Surfaces – SMS 2021
Onsite Session I

Thermomagnetic Energy Harvesting: From Material Properties to Engineering of Functional Devices

M. Kohl

Karlsruhe Institute of Technology KIT, Institute of Microstructure Technology, Karlsruhe, Germany

Abstract:

The demand for power generation in remote or hardly accessible sites is constantly rising due to global trends like wireless sensor networks and autonomous electronic devices. Energy harvesting plays an important role as an enabling technology to avoid usage of cables or batteries. Recovery of thermal energy is of particular interest as waste heat is a growing and abundant energy resource. Much of the unrecovered waste heat is in the low temperature regime below 250 °C, while energy conversion becomes inefficient at low temperature differences [1]. Miniaturization of state-of-the art thermo-electric generators is limited as active heat sinking beyond natural convection is required. This disadvantage is avoided in miniature TMG devices using the novel concept of resonant self-actuation [2]. In this case, the performance of TMG devices relies on the large temperature-dependent change of magnetization in Heusler alloy films due to a martensitic transformation and/or ferromagnetic transition. Fig. 1 illustrates the layout and operation principle for the case of a TMG with a ferromagnetic NiMnGa film. Due to the film's large surface-to-volume ratio, efficient heat transfer at contact to the magnet and active cooling are possible via heat conduction in the cantilever and forced air convection due to rapid oscillatory motion. Thereby, resonant oscillation is maintained as long as the temperature-induced change of magnetic actuation force is larger than the losses during oscillation.

TMG film devices operate at resonance frequencies of typically 80 Hz and reach power densities up to 120 mW/cm^3 [2]. Reaching high power output requires detailed understanding and control of the conditions of resonant self actuation, which is governed by the complex coupling of the thermo-magneto-mechanical properties in the system [2,3]. Currently, next generation TMG film devices are being developed concentrating on upscaling with respect to thickness [3] and footprint [4]. Another ambitious goal is the development of optimized thermomagnetic materials with low transition temperatures to enable recovery of low-grade waste heat close to room temperature.

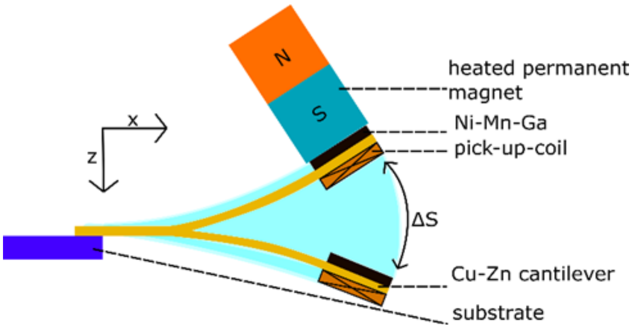


Figure 1: Layout and operation principle of a TMG device using a Ni-Mn-Ga film at the cantilever front for resoant self-actuation. A pick-up coil is used for power conversion according to Faraday's law.

Keywords: Thermomagnetic energy harvesting; power generation; waste heat recovery; magnetic shape memory films; Ni-Mn-Ga film; magnetic phase transition; Curie temperature.

References:

1. Bucsek, A.N., Nunn, W., Jalan, B., James, R.D. (2020), Energy Conversion by Phase Transformation in the Small-Temperature Difference Regime, *Annu. Rev. Mater. Res.*, 50, 1–36.
2. Gueltig, M., Wendler, F., Ossmer, H., Ohtsuka, M., Miki, H., Takagi, T., Kohl, M. (2017), High-Performance Thermomagnetic Generators Based on Heusler Alloy Films, *Adv. Energy Mater.*, 7, 1601879.
3. Joseph, J., Ohtsuka, M., Miki, H., Kohl, M. (2020), Upscaling of Thermomagnetic Generators Based on Heusler Alloy Films, *Joule*, 4, 2718–2732.
4. Joseph, J., Wehr, M., Miki, H., Ohtsuka, M., and Kohl, M. (2021), Coupling effect in parallel thermomagnetic generators based on resonant self-actuation, Proc. of the 21st Int. Conf. on Solid-State Sensors, Actuators and Microsystems, Transducers'21, online virtual conference, 20-25 June 2021.

MAMS – the 3rd generation of electromechanical devices

K. Ullakko, V. Laitinen, A. Saren and O. Sozinov

LUT University School of Engineering Science, Finland

Abstract:

In recent years, micro-electromechanical systems (MEMS) have been developed for optical, microfluid and sensor applications. In this presentation, a new concept of micro-magnetomechanical systems (MAMS) made of an adaptive MSM (Magnetic Shape Memory) material will be introduced. MAMS will represent the 3rd generation of devices in the evolution of electromechanics. The 1st generation devices are made from construction materials and they contain separate machine components. The 2nd generation devices, e.g., MEMS, are made from functional materials like silicon. The 3rd generation devices will be manufactured from adaptive materials. MAMS devices contain actuators, sensors, gripper, switches, valves, pumps, fluid channels and other functional components as integrated parts of the device. In this presentation, the first steps in making the MAMS devices using additive manufacturing and laser ablation will be presented. MAMS devices enable more complex geometrical designs and higher functionality than MEMS devices made from silicon. Some zones in the MAMS devices can be made for generating motion (active zone) and other zones for performing other functions (passive zone). Active and passive zones are prepared to have proper twin structures, so that active zones have a dense twin structure enabling a smooth straining by an applied magnetic field while in passive zones, twin boundary mobility is entirely prevented. MSM materials are suitable for the MAMS devices due to their ultrafast actuation of over 2 million m/s2 and large magnetic-field-induced strains up to 11%. Preliminary modeling results on the interaction of MAMS devices with fluids will be presented. Ultrafast dynamics of the MAMS devices is expected to enable new discoveries in fluid dynamics, chemistry and biomedicine.

Structures of ice confined in nanopores ; pressure enhancement and wetting energy effects

M. Śliwinska-Bartkowiak[1*], M. Jazdzewska[1], K.Rotnicki[1], A.Beskrovny[2], K. E. Gubbins[3]

[1] Faculty of Physics, Adam Mickiewicz University, Poznan, Poland
[2] Joint Institute for Nuclear Research, Dubna, Russia
[3] Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, USA

Abstract:

We report X –rays diffraction studies of water adsorbed in nanoporous activated carbon fibres (ACFs) and CMK-3 and CMK-8 carbon mesopores of different pore sizes. The fibres are built of turbostratic nanoparticles separated by quasi two-dimensional voids, forming narrow slit-shaped pores; CMK-3 and CMK-8 are the reverse carbon replica of silica SBA-15 and KIT-6 porous matrices. In order to determine the structure of water within the pores and its influence on the fibres' structure, mean interatomic and intermolecular distances have been estimated from the positions of the maxima of the normalized angular distribution functions obtained by X-ray diffraction [1]. We observe significant changes in the interlayer distance of the carbon nanoparticles; the results suggest that very high pressures arise within the pores,of the order a few hundreds MPa, as has been observed in molecular simulations [1,2]. Such results are confirmed by observation of high pressure forms of ice in cylindrical nanocarbons , using neutron and X –ray diffraction [2]. For water in multi-walled carbon nanotubes (MWCN), below the pore melting point cubic ice was observed. This structure of ice can be obtained during re-crystallisation from high pressure phases at low temperature for the ice bulk. For CMK-3 and CMK-8 mesopores we observed the existence of a stacking-disordered ice, $\mathrm{I_{sd}}$ [4,5]. This metastable ice is neither cubic nor hexagonal, and is not a simple mixture of the two, but a combination of cubic sequences intertwined with hexagonal sequences, which was identified as having the space group p3m1 [3]. Moreover, the stacking disorder can vary in complexity depending on the way the ice is formed and on the prevailing thermal conditions during this process. It strongly depends of the wetting energy of the pore walls [5] An analysis of the kind of $\mathrm{I_{sd}}$ formed in CMK-3 and CMK-8 of different pore sizes and also in ACF will be presented .

The wetting energy of water on pore walls for the systems studied will be also considered. Observed crystal forms, which occur in bulk ice only at temperatures below 180 K in the case of cubic ice, and at pressures of hundreds or thousands of MPa are stabilized by the confinement.

Keywords: nanoporous matrices, confined ice, X-rays and neutrons diffraction, wetting energy, high pressure forms of ice in nanopores

References:

1. M.Sliwinska-Bartkowiak, M.Drozdowski, M.Jazdzewska, Y.Long, J.Palmer, K.E.Gubbins,(2013) *Phys. Chem. Chem. Phys.*, **14**, 71454.
2. Y. Long, J.Palmer, B.Coasne, M.Sliwinska-Bartkowiak, K.E.Gubbins (2011) *Phys.Chem.Chem.Phys* 14,17163; M.Jazdzewska , M. Sliwinska- Bartko wiak, A. Beskrovny, S.G. Vasilovskiy, K.Gubbins at al (2011) *Phys. Chem. Chem. Phys*, 13,7008
3. Malkin, T. L., Murray, B. J., Salzmann, C., Molinero, V., Pickering, S. (2014) *Phys. Chem. Chem. Phys*.,17,6076; A.Haji-Akbari, P.G.Debenedetti(,2015) *PNAS*, **112,** 10582
4. K.Domin,K.Y.Chan,H.Yung, K.E.Gubbins, M. Sliwinska-Bartkowiak (2016), *J.Chem..Eng. Data*, **61**, 4252-4260,
5. M.Jazdzewska, M.Sliwinska-Bartkowiak, K.Domin, A.Beskrownyi, (2019), *J.Mol.Liquids*, 283, 167-173,

Financial support from the National Centre of Science, grant No. UMO-2016/22/A/ST4/00092 is gratefully acknowledged.

The role of long-range electrostatic interactions and local topology of the hydrogen bond network in the wettability of fully and partially wetted single and multilayer graphene

Mara Chiricotto[1], Fausto Martelli[2,3], Giuliana Giunta[1], Paola Carbone[1]

[1]Department of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, M13 9PL, Manchester, United Kingdom
[2]IBM Research Europe, WA4 4AD, Daresbury, United Kingdom
[3]Department of Physics and CNR-Institute of Complex Systems, Sapienza University of Rome, P.le Aldo Moro, I-00185 Roma, Italy

Abstract:

The wetting properties of graphene and other 2D materials is a new rising field due to its wide technological repercussions, such as desalination membranes, sensors, and coating from electrochemical degradation, promotive coating for dropwise condensation. Recently, both experimental and theoretical studies have contributed in deepening our understanding of this important field, but basic questions still remain unanswered. In particular, the role of separate interactions driving wetting properties remains an intricate puzzle, and the organization of water molecules in the proximity of the surfaces, unexplored.

In this talk we present a computational method for the estimation of interfacial energies and wetting properties of water/graphitic interfaces with a special focus on fully and partially wetted (i.e., in contact with water on one side and vacuum on the other) single and multilayer graphene.

Through the calculation of the local stress tensor based on the Irving-Kirkwood-Noll theory we rationalize the role of van der Waals and electrostatic interactions in the wettability. While van der Waals interactions dominate in the partially wetted system (in agreement with previous results), we have found that the wettability of fully wetted graphene is a balance between van der Waals and electrostatic interactions. In both cases we relate the strength of such interactions with the modification of the hydrogen bond network, coordination defects and diffusion in the proximity of the surface. We then propose a set of valuable tools to investigate the effect of long-range electrostatic and dispersive contributions on the wetting phenomena and their effects on the local structure. The investigation of the wettability of graphene and graphite is an important aspect in predicting the behaviour of aqueous solutions under nanoconfinements, the permeability of porous materials, the interactions among graphitic surfaces and their dispersion in aqueous environments. Therefore, our results can be applied to the interface-related phenomena to better understand the interface where the local energy varies at the nanoscales

Keywords: Graphene, Water, Wettability, Surface Tension, Local Stress profile, Hydrogen Bond Network

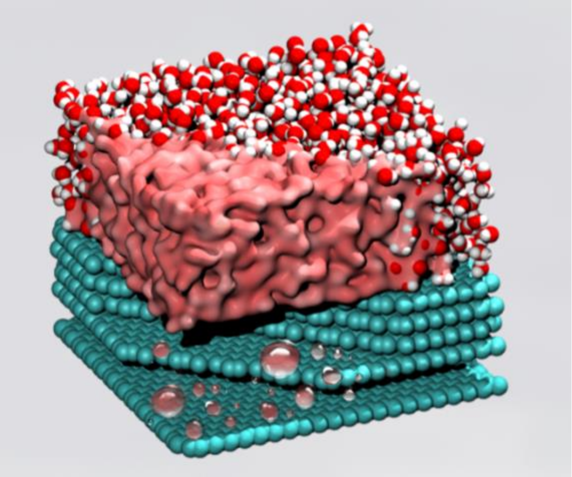


Figure 1: Figure illustrating multilayer graphene wetted by water.

References:

1. M. Chiricotto, G. Giunta, H. A. Karimi-Varzaneh & P. Carbone (2020), Soft Materials, 18:2-3, 140-149, (2019).
2. Formanek, M. & Martelli, F. AIP Adv. 10, 055205 (2020).
3. Martelli, F., Crain, J. & Franzese, G. ACS Nano 14, 8616–8623 (2020)

Buckle depression as a signature of the elastic properties of 2D materials

C. Coupeau

Pprime Institut, Dpt of Physics and Mechanics of Materials, University of Poitiers/CNRS/ENSMA, France, christophe.coupeau@univ-poitiers.fr

Abstract:
Thin films and coatings are used in a wide range of technological applications. They often develop high residual stresses, for instance during the deposition process, sometimes about few GPa in compression. Such large compressive stresses may cause the nucleation and growth of buckling structures [1] that generally result in the loss of functional properties that were initially conferred to such film/substrate composites.

The fine investigation of the morphology of the buckling structures can be however of great interest in order to quantitatively extract some physical/mechanical parameters of the coated materials. In the case of a high elastic contrast between a rigid film and a soft substrate (high Dundurs' coefficient α), it is shown that the straight-sided buckle presents a small depression on both edges at the nanometer scale (Fig. 1) [2,3]. Finite element simulations have shown that $\delta_2=0$ as expected for a rigid substrate ($\alpha=-1$) and continuously increases with the increase of α up to +1. The Dundurs's coefficient α was numerically observed to evolve as follows [4] :

$$\alpha = \frac{\lambda^3 - 1}{\lambda^3 + 1}$$

with $\lambda = 3.75(b/h)(\delta_2/\delta_1)^{2/3}$. It is interesting to note that λ can be directly determined experimentally from the investigation of single buckles, for instance with the help of atomic force microcopy.

2D materials, such as graphene or MoS_2, deposited or synthesized on metallic subtrates are known to exhibit a high elastic contrast. It is thus believed that spontaneous as-grown or thermally-mechanically-induced buckles will be a relevant morphological signature of the Young modulus of this new class of materials. The method can offer an interesting alternative in the case of rigid materials on soft substrates, for which the usual nano-indentation technique may be difficult to implement.

Keywords: 2D materials / Elastic properties / Stress / Buckling

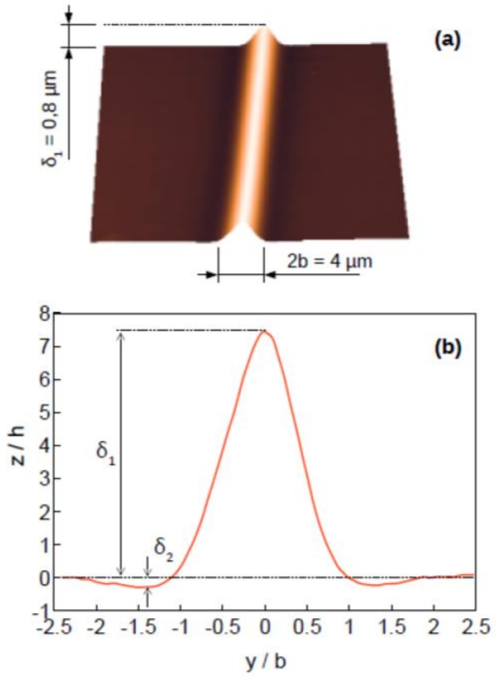


Figure 1: Characteristic profile of a Ni/Polycarbonate (α=+0.97) buckle showing a nanometer scale depression at the buckle edges. a) AFM image of a straight-sided buckle of width 2b=4µm and thickness h=100 nm. b) Normalized out-of-plane displacement vs. normalized position. δ_1 and δ_2 correspond to the maximum deflection of the buckle and the depression, respectively.

References:

1. G. Parry, A. Cimetière, C. Coupeau, J. Colin, J. Grilhé, Phys. Rev. E 74 (2006) 1539.
1. G. Parry, J. Colin, C. Coupeau, F. Foucher, A. Cimetière, J. Grilhé, Acta Mater. 53 (2005) 441.
2. R. Boijoux, G. Parry, J.-Y. Faou, C. Coupeau, Appl. Phys. Lett. 110 (2017) 141602.
3. R. Boijoux, G. Parry, C. Coupeau, Thin Solid Films 645 (2018) 379.

Tailor-Making Nano Insulation Materials through Synthesis of Hollow Silica Nanospheres

Bjørn Petter Jelle [1,*], Sohrab Alex Mofid [1]
[1] Norwegian University of Science and Technology (NTNU),
Department of Civil and Environmental Engineering, NO-7491 Trondheim, Norway.
[*] Corresponding and presenting author: bjorn.petter.jelle@ntnu.no (e-mail).

Abstract:
As the world of today is turning its focus even more towards aspects like energy efficiency and renewable and non-polluting energy harvesting, including the building sector, the quest has been set for developing high-performance thermal insulation materials with very low thermal conductivities. In this respect, a possible and promising pathway to achieve these thermal super insulation materials (SIM) is to utilize the Knudsen effect where the pore diameters of these materials are attempted lowered below the mean free path of the air molecules, i.e. in the nanorange, thus creating a nano insulation material (NIM) with a nanoporous structure. A particular pathway to manufacture a NIM is to fabricate hollow silica nanospheres (HSNS) by a sacrificial template method, where one may tailor-make the HSNS by controlling their inner sphere diameter and shell thickness. Hence, one may then in principle also be able to tailor-make HSNS with the desired thermal conductivity, normally with as low thermal conductivity as possible. This study will present our latest experimental results with these NIMs made through HSNS, demonstrating a decreasing thermal conductivity with a decreasing inner sphere diameter. These experimental results are also compared with theoretical predictions by the Knudsen effect. In general, miscellaneous pathways are possible when attempting to make NIMs. Herein, we are reporting the results from applying the sacrificial template method for fabricating HSNS. The sacrificial template spheres have so far in our experimental investigations mainly been made as either polyacrylic acid (PAA) or polystyrene (PS) template spheres. The silica source has in general been the silica precursors tetraethyl orthosilicate (TEOS) and water glass (Na_2SiO_3), and in particular TEOS for the main results reported within this study. After the PAA or PS templates have been coated with a layer of silica, either in the form as small silica particles or as a large, wrinkled silica sheet (e.g. depending on the silica precursor), the PAA or PS templates have been removed. In this process the PAA templates have been removed by chemical treatment/washing and the PS templates have been removed by heat treatment, where the template materials have been diffusing and evaporating through the silica shells. The final manufactured result is then a potential NIM in the form of HSNS. In principle, the HSNS synthesis process by the sacrificial template method is depicted in the cross-section illustration alongside an actual example of HSNS synthesis as given in Fig.1 with scanning electron microscope (SEM) images of synthesized spherical PS templates, a PS template coated with small silica particles, and HSNS after removal of the PS templates, thus demonstrating a captivating and enchanting example of the scientific step from theoretical concepts to actual experimental results. From the experimental investigations it is seen that the measured thermal conductivity decreases with decreasing HSNS inner diameter, which is also predicted by the Knudsen effect. Furthermore, it is also observed that for an inner sphere diameter reduction of HSNS from 213 nm to 85 nm, the measured thermal conductivity is reduced from 29.7 mW/(mK) to 14.3 mW/(mK), respectively.

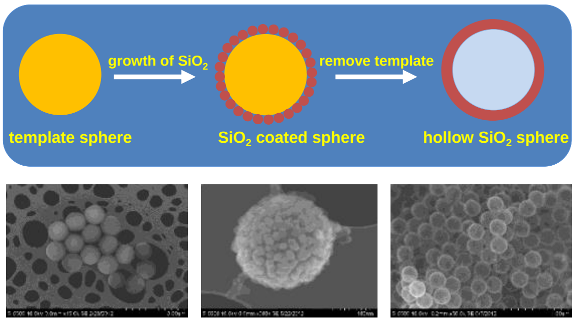


Figure 1: (Top) Illustrated cross-section of the hollow silica nanospheres (HSNS) synthesis process by the sacrificial template method. (Bottom) SEM images of an actual HSNS synthesis process with (left) spherical PS templates, (middle) small silica particles coated around a spherical PS template, and (right) HSNS after removal of PS templates.

Keywords: nano insulation material, NIM, hollow silica nanosphere, HSNS, super insulation material, SIM, thermal insulation, thermal conductivity, Knudsen effect.

Martensitic microstructures in nanocrystalline NiTi wires thermomechanically loaded in tension

P. Šittner[1*], O.Molnárová[1], L.Heller[1], H.Seiner[2]
[1] Institute of Physics of the CAS, Na Slovance 1992/2, 18221 Prague, CR
[2] Institute of Thermomechanics of the CAS, Dolejškova 5, Prague, CR

Abstract:

Superelasticity and shape memory effects in NiTi shape memory alloys undergoing cubic to monoclinic martensitic transformation upon thermomechanical loading involve restoration of the original parent austenite crystal structure and material strain state in a complete thermomechanical load cycle across transformation range. Ideally, the martensitic transformation proceeding in a closed loop thermomechanical loading cycle does not generate unrecovered strains and does not leave behind any permanent lattice defects in the austenitic microstructure. If, however, plastic deformation occurs during the closed loop cycle, unrecovered strain is recorded and the austenitic microstructure of deformed alloy contains permanent lattice defects. How the unrecovered strains are generated and how the permanent lattice defects are created remains to be a puzzle since the plastic deformation processes occur in the martensite state.

In order to characterize the transformation/reorientation as well as plastic deformation processes in the martensite phase of nanocrystalline NiTi wires, we performed series of closed loop thermomechanical loading tests involving tensile deformation at three test temperatures, determined recoverable and unrecovered strains and reconstructed martensite variant microstructures in selected grains (orientation, size and location of martensite variants and intervariant interfaces) evolving during the test by employing selected area electron diffraction with dark field image analysis method in TEM [1].

The analysis (Fig. 1) have shown that NiTi wire deformed up to the end of reorientation (transformation) plateau contains single domain of (001) compound twinned B19' martensite filling whole grains of the deformed wire. On further tensile loading beyond the yield stress up to 15% strain, plastic deformation of the twinned martensite proceeds by combined (100) and (20$\bar{1}$) deformation twinning assisted by [1 0 0](0 0 1) dislocation slip in oriented martensite alongside the detwinning of (001) compound twins. This peculiar deformation mechanism gives rise to martensitic microstructures containing (100) and (20$\bar{1}$) deformation twins in largely detwinned martensite matrix. Upon subsequent unloading and stress free heating above the A_f temperature, this martensitic microstructure transforms to {114} twinned austenitic microstructure. This deformation mechanism renders NiTi excellent combination of strength and deformability and leads to extreme refinement of the austenitic microstructure of the deformed wire.

Keywords: Martensitic transformation, nanocrystalline NiTi, martensitic microstructures, transformation electron microscopy

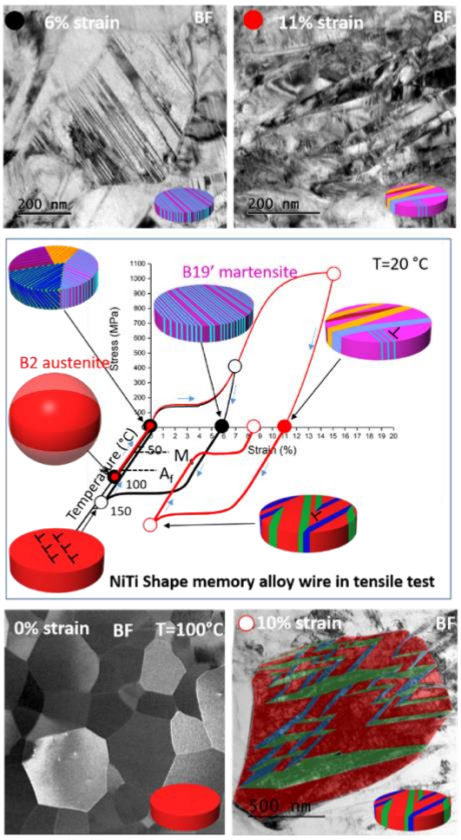


Figure 1: Evolution of martensitic microstructures during tensile thermomechanical loading of nanocrystalline NiTi shape memory wire.

References:

1. Molnárová, O.,Tyc,O., Heller L., Seiner,H. Sittner, P. Evolution of martensitic microstructures in nanocrystalline NiTi wires deformed in tension. Acta Materialia (2021) under review, available at SSRN: https://ssrn.com/abstract=3797420

Viologen π-Dimerization as a Trigger for Metamorphism in Supramolecular Stimuli-Responsive Materials

D. Frath[1], T. Gibaud[2], S. Chowdhury[1], C. Kahlfuss[1], C. Roizard[1], A. F. Carreira[1], R. Grüber[1], Y. Nassar[1], L. Guy[1], F. Chevallier[1], E. Dumont[1], A. P. Ramos[3], G. J.-F. Demets[3], E. Saint-Aman[4], C. Bucher[1]
[1] Laboratoire de Chimie, ENS Lyon, CNRS UMR 5182, Lyon, France
[2] Laboratoire de Physique, ENS Lyon, CNRS UMR 5672, Lyon, France
[3] DQ-FFCLRP, Universidade de São Paulo, Ribeirão Preto, Brazil
[4] Univ. Grenoble Alpes, CNRS, Département de Chimie Moléculaire, Grenoble, France

Abstract:

The key elements in the development of nanoscience are to observe, modify and control mater at the nanoscale. One strategy proposed to meet these immense challenges is to develop responsive molecular or supramolecular systems for which a structural reorganization is obtained when exposed to an external stimulus: this phenomenon is known as *metamorphism*. Systems that endure structural changes leading to major modification of macroscopic properties are of great interest for the controlled capture and release of guest molecules, the development of molecular machines and molecular electronics.

The strategy developed at the Chemistry Laboratory of ENS Lyon is to exploit the switching and assembly properties of π-conjugated organic radicals that can be generated in-situ by electrical or light excitation.[1-3] This concept is based on molecular or supramolecular engineering strategies aiming at promoting the formation of π-dimers in solution under usual conditions of temperature and concentration. A first approach consists in favoring the formation of π-dimers inside cavitands molecules such as cucurbituril in order to control the reversible association/dissociation of molecular building blocks into 2D-supramolecular assembly.[1] Another approach consists in connecting viologen subunits by labile coordination bond or with mobile covalent linker in order to guide and facilitate an electron-transfer triggered switching.[2,3] These strategies are very promising for the development of new soft-materials such as gels with switchable properties.[3]

Keywords: viologen, π-dimerization, metamorphism, metamorphism, spectroscopy, electrochemistry, stimuli-responsive materials, supramolecular gels.

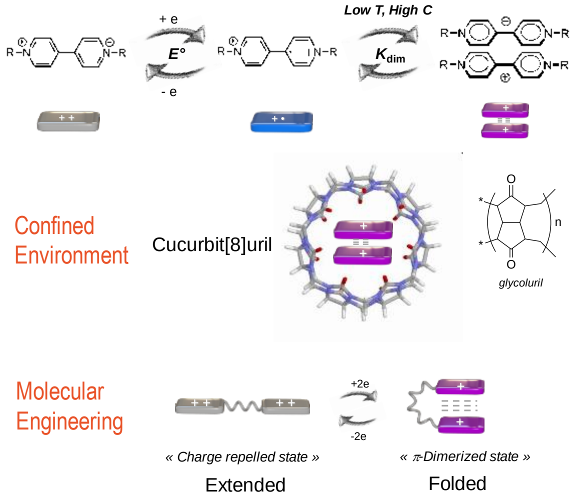


Figure 1: Figure illustrating the π-dimerization of viologen derivatives.

References:

1. Chowdhury, S.; Nassar, Y.; Guy, L.; Frath, D.; Chevallier, F.; Dumont, E.; Ramos, A. P.; Demets, G. J.-F.; Bucher, C. Photo/Redox-Responsive 2D-Supramolecular Assembly Involving Cucurbit[8]Uril and a Star-Shaped Porphyrin Tecton. *Electrochim. Acta* **2019**, *316*, 79–92.
2. Kahlfuss, C.; Chowdhury, S.; Carreira, A. F.; Grüber, R.; Dumont, E.; Frath, D.; Chevallier, F.; Saint-Aman, E.; Bucher, C. Electron-Triggered Metamorphism in Palladium-Driven Self-Assembled Architectures. *Inorg. Chem.* **2021**, *60* (6), 3543–3555.
3. Kahlfuss, C.; Gibaud, T.; Denis-Quanquin, S.; Chowdhury, S.; Royal, G.; Chevallier, F.; Saint-Aman, E.; Bucher, C. Redox-Induced Molecular Metamorphism Promoting a Sol/Gel Phase Transition in a Viologen-Based Coordination Polymer. *Chem. Eur. J.* **2018**, *24* (49), 13009–13019.

Analytical, Numerical and Experimental Study of the Self-Heating of a Shape Memory Composite

C. A. Pereira Sánchez[1,*], M. Houbben[2], J. F. Fagnard[1], P. Laurent[1], C. Jérôme[2], L. Noels[3] and P. Vanderbemden[1]
[1] Department of Electrical Engineering and Computer Science, University of Liège, Liège, Belgium
[2] CERM, CESAM-RU, University of Liège, Liège, Belgium
[3] Department of Aerospace and Mechanical Engineering, University of Liège, Liège, Belgium

Abstract:

Shape memory polymers (SMP) and their composites (SMC) are smart materials having morphing capabilities that are applied in several fields such as aerospace, biomedical or textile engineering [1]. Among the possible shape change triggering methods, electroactive SMC have steadily gained interest within the range of shape memory materials in the recent years due to the fast and efficient triggering through Joule resistive heating. During this process, the heat is generated directly within the material. However, in order to produce a well-defined shape change, the temperature increase resulting from self-heating should be accurately predicted. The temperature is time-variant and non-uniform within the material. This directly affects the amount of heat generated since the electrical resistivity is, in general, found to be dependent on the local temperature of the SMC [2].

In this study we examine in detail the self-heating phenomenon of an electroactive SMC when an electric current is injected at constant power. The study aims at identifying the parameters that are crucial for predicting the temperature increase and at understanding how any variation of them affects the self-heating process. The SMC is chemically crosslinked poly(ε-caprolactone) filled with 3 wt% of multiwall carbon nanotubes. The self-heating phenomenon is studied by means of analytical formulas, a 3D thermo-electric numerical model and surface temperature measurements (figure 1). We derive analytical expressions of the 2D temperature distribution within a parallelepipedic SMC, either with constant or linearly-dependent electrical resistivity. The analytical expressions are able to reproduce the principal features of the temperature distribution across the sample. The temperature increase depends on many parameters related to the heat transfer process, both within the SMC and at the interface between the SMC and its environment. The results show that, for this particular SMC, the temperature dependence of the resistivity has little effect on the final temperature, whereas the thermal conductivity plays a significant role. The transient characteristics of the temperature evolution are shown to be influenced by the highly non-linear temperature dependence of the heat capacity. The self-heating phenomenon appears to also be strongly dependent on the contact with external objects, such as clamps or grips, that are frequently used during the shape memory cycles.

Keywords: shape memory, composites, smart materials, carbon nanotubes, self-heating, electroactivation

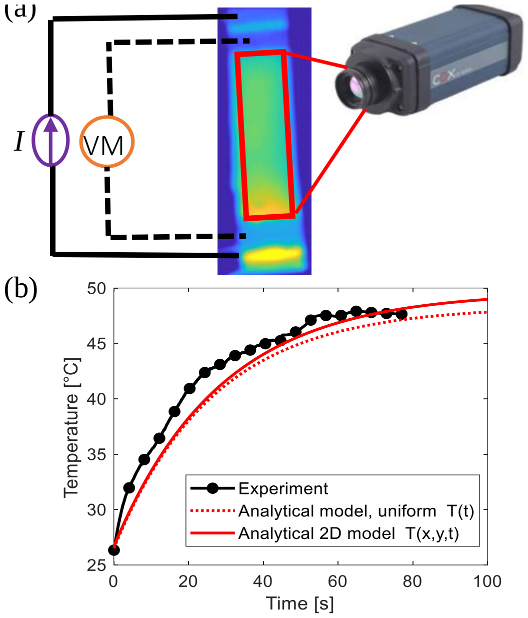


Figure 1: (a) Example of surface temperature measurement, (b) time evolution of the temperature obtained experimentally and analytically.

References:

1. Melly, S. K., Liu, L., Liu, Y., Leng, J. (2020), Active composites based on shape memory polymers: overview, fabrication methods, applications, and future prospects, *J. Mater. Sci.*, 55, 10975-11051.
2. Taherian, R., Ghorbani, M., M. (2017), Investigation of the electrical properties of polymer/carbon composites exposed to Joule heating and heat treatment, *ESC J. Solid. State Sci. Technol.*, 6, 3019-3027

Landau-energy Landscape Reconstruction for a Ni-Fe-Ga(Co) Shape Memory Alloy

H. Seiner[1,*], K. Zoubková[2], P. Sedlák[1], E. Villa[3], M. Tahara[4], H. Hosoda[4], V. Chernenko[4,5,6]
[1] Institute of Thermomechanics, Czech Academy of Sciences, Prague, Czech Republic
[2] FNSPE, Czech Technical University in Prague, Prague, Czech Republic
[3] CNR ICMATE Sede di Lecco, Lecco, Italy
[4] Institute of Innovative Research (IIR), Tokyo Institute of Technology, Yokohama, Japan
[5] BCMaterials & University of Basque Country (UPV/EHU), Bilbao, Spain
[6] Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Abstract:
Elastic behavior of single crystals of Ni-Fe-Ga(Co) ferromagnetic shape memory alloys was studied in a broad temperature range. Using tensile stress-strain measurements and ultrasonic characterization, we proved that austenite and martensite phases of the given alloy exhibit strongly non-linear elastic responses, and we utilized the non-linear stress-strain data for constructing an energy function describing the observed behavior within the framework of the 4th-order Landau theory.

In this contribution, we will show that the resulting energy landscape captures realistically several key features of the examined alloy, such as the existence of the critical point indicated by the extrapolation of the stress-strain data, or the value and temperature dependence of the transformation strain. Explicit formulas for the energy landscape will be provided, using linear and quadratic approximations to express the temperature evolution of the Landau-energy parameters.

Keywords: Shape memory alloys, Landau theory, non-linear elasticity, postcritical behavior.

References:

1. Kosogor, A. L'vov, V.A., Chernenko, V., Villa, E., Barandiaran, J.M., Fukuda, T., Terai, T., Kakeshita, T. (2014), Hysteretic and anhysteretic tensile stress-strain behavior of Ni-Fe(Co)-Ga single crystal: Experiment and theory, *Acta Mater.*, 66, 79-85.

2. Zoubková, K., Seiner, H., Sedlák, P., Villa, E., Tahara, M., Hosoda, H., Chernenko, V. (2021) Non-linear elastic behavior of Ni-Fe-Ga(Co) shape memory alloy and Landau-energy landscape reconstruction, submitted to *Acta Mater.*

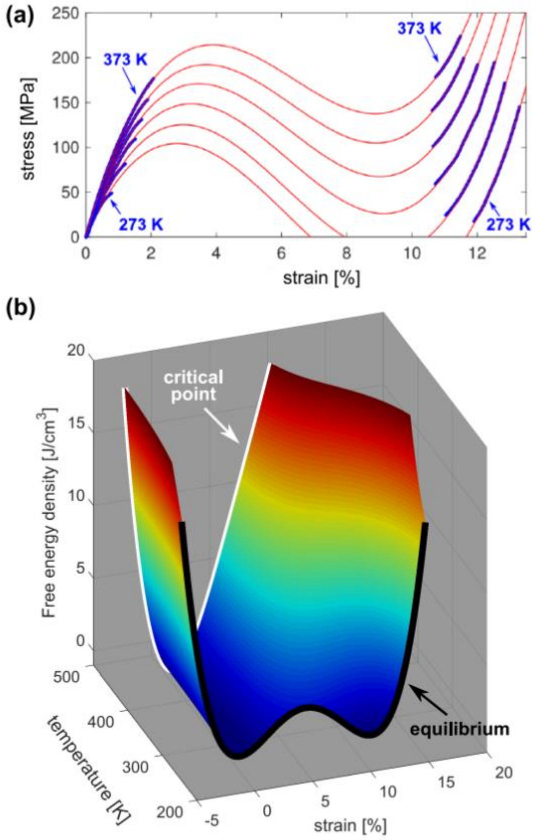


Figure 1: Fitting of the stress-strain curves by Landau-theory polynomial approximations (a) and the reconstructed energy landscape (b) for a single crystal of the Ni-Fe-Ga(Co) alloy loaded by uniaxial tension along the [001] direction.

Localization of Martensitic Transformation in NiTi Shape Memory Alloys: Experimental Observations by 3D Diffraction/Scattering Computed Tomography and Numerical Reconstruction

P. Sedlak [1*], M. Frost [1], H. Seiner [1], P. Sittner [2]
[1] Institute of Thermomechanics, CAS, Prague, Czech Republic
[2] Institute of Physics, CAS, Prague, Czech Republic

Abstract:

The stress-induced martensitic transformation in polycrystalline NiTi-based shape memory alloys (SMA) often tends to localize in bands on the macroscopic scale. These ‘‘martensitic bands” form within the austenitic sample and the transformation propagates by their multiplication and/or by movement of their fronts, similarly to the well-known Lüders bands of plastic deformation in some metallic materials. If the localization appears, it has a serious impact on the thermomechanical response, e.g., via pronounced heterogeneity of stress and strain or via spatially heterogeneous latent heat release or absorption. Localization has been also found critical for the failure of NiTi polycrystalline structures.

In this work, we firstly show a detailed experimental reconstruction of macroscopic austenite–martensite transition zones in thin superelastic NiTi wires subjected to stretching, twisting and their combination obtained by diffraction/scattering computed tomography (DSCT). The method allows to visualize spatial distributions of both phases from a series of X-ray diffraction scans. A cone-shaped, radially symmetric transformation front was observed in stretched wire both with and without applied pre-twist. Twisting of a pre-stretched wire (with a cone-shaped transformation band front already developed) led to the formation of a multi-prong localization morphology recognizable on the surface (Figure 1). Transition zones in these cases are highly heterogeneous complex 3D objects exhibiting distinct phase gradients; the longitudinal size of the zones is comparable with the wire diameter. In contrast, localized martensitic strips parallel with wire axis and with a wedge-like cross-section appeared on the surface of the wire which was twisted only [1].

Taking into account the experimental findings, we have adapted our macroscopic constitutive model of NiTi SMA by modifying the internal energy term and including non-local (gradient-like) effects [2]. The finite element implementation of the model into Abaqus FEA software allowed successful reconstruction of the transformation front in a loaded wire in pure tension, however, a successful numerical reconstruction of longitudinal martensitic bands formed in torsion is challenge for further model development.

Keywords: shape memory alloys, NiTi, localization, FEM simulation, 3D-XRD, diffraction/scattering computed tomography

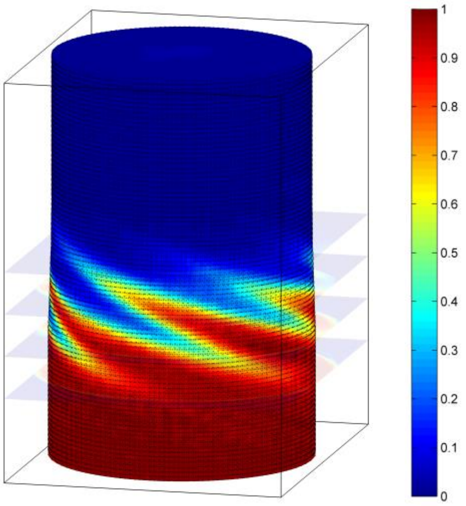


Figure 1: A multi-prong localization morphology of austenite–martensite transition zone after twisting of a pre-stretched wire – experimental reconstruction of austenite volume fraction by 3D DSCT.

References:

1. Sedlák P., Frost M., Ševcik M., Seiner H. (2021) 3D spatial reconstruction of macroscopic austenite–martensite transition zones in NiTi wires induced by tension and twisting using diffraction/scattering computed tomography, *International Journal of Solids and Structures* 228,111-122.
2. Frost, M., Benesova, B., Seiner, H., Kruzik, M., Sittner, P. (2021) Thermomechanical model for NiTi-based shape memory alloys covering macroscopic localization of martensitic transformation, *International Journal of Solids and Structures* 221, 117–129.

Ultrasonic-based evaluation of the NiTi shape-memory alloy elasticity during stress-induced martensitic transformation

T. Grabec, P. Sedlák, K. Zoubková, P. Stoklasová, M. Ševčík, M. Janovská, H. Seiner
Institute of Thermomechanics, Czech Academy of Sciences, Prague, Czechia

Abstract:

A polycrystalline NiTi sample was studied during pseudoplastic straining. Various ultrasonic methods were utilized to measure velocities of bulk and surface acoustic waves in several directions with respect to the mechanical loading. Using a numerical inverse procedure, a full elastic tensor of the transversely isotropic polycrystal during the stress-induced austenite→R-phase→martensite transformation was obtained. The evolution of the sample's elasticity revealed an unexpectedly strong anisotropy of the R-phase already in the low-strain state, which was then retained in character throughout the transformation and even in the stress-free oriented martensite after unloading.

The knowledge of the full elasticity allowed for a creation of a micromechanical model based on homogenization approaches, which led to the conclusion that the strong anisotropy was not caused predominantly by the anisotropy of the unit cell and the crystallographic texture but was rather related to twin boundaries both in the R-phase and in martensite. This conclusion may provide an important link to explain the up-to-date discrepancy between the *ab initio* calculations and experimental results.

Keywords: NiTi, Shape-memory alloy (SMA), martensitic transformation, ultrasonic characterization, anisotropic elasticity.

References:

1. Grabec, T., Sedlák, P., Zoubková, K., Ševčík, M., Janovská, M., Stoklasová, P., Seiner, H. (2021) Evolution of elastic constants of the NiTi shape memory alloy during a stress-induced martensitic transformation, *Acta Mater.*, 208, 116718.
2. Thomasová, M., Seiner, H., Sedlák, P., Frost, M., Ševčík, M., Szurman, I., Kocich, R., Drahokoupil, J., Šittner, P., Landa, M. (2017) Evolution of macroscopic elastic moduli of martensitic polycrystalline NiTi and NiTiCu shape memory alloys with pseudo-plastic straining, *Acta Mater.*, 123, 145-156.

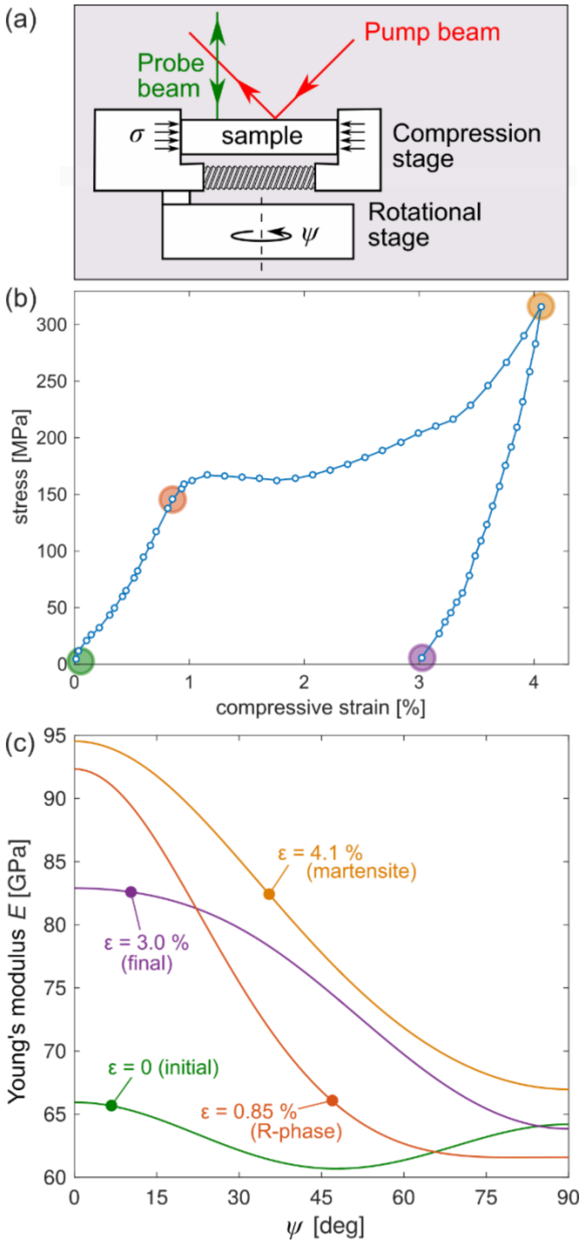


Figure 1: (a) Diagram of the laser-ultrasonic experimental setup for the surface-wave velocity measurement, showing the geometry of the mechanical loading with respect to the laser beams; (b) stress-strain response of the sample in compression at room temperature; (c) directional dependence of Young's modulus at the strain stages distinguished in (b), with 0° corresponding to the loading axis.

Correlation between microstructural condition and functional and magnetic properties in sintered $Ni_{50}Mn_{30}Ga_{20}$ ferromagnetic shape memory alloy

F. Villa [1,*], A. Nespoli [1], C. Fanciulli [1], F. Passaretti [1], F. Albertini [2] and E. Villa [1]

[1] Consiglio Nazionale delle Ricerche – Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia (CNR – ICMATE Sede di Lecco) via G. Previati, 1/E, 23900 Lecco (Italy)
[2] Consiglio Nazionale delle Ricerche – Istituto dei Materiali per l'Elettronica ed il Magnetismo (CNR – IMEM) Parco Area delle Scienze 37/, 43124 Parma (Italy)

Abstract:

Among ferromagnetic shape memory alloys (FeSMAs), NiMnGa system attracts particular attention thanks to the extremely large magnetic-field-induced strain (MFIS) caused by the rearrangement of the twin boundaries induced by an applied magnetic field. Moreover, the modulation of the microstructure of polycrystalline NiMnGa alloys has been investigated to improve their functional properties and to reduce their typical brittleness. For this reason, increasing interest has been devoted to different kinds of sintering routes for the fabrication of this material; in the present study, $Ni_{50}Mn_{30}Ga_{20}$ alloy was produced by means of the open die pressing (ODP) process. This sintering method was chosen as an alternative and low-cost method for the consolidation of NiMnGa powders and the effects of the process parameters such as sintering time, cooling method, and applied thermal treatments were investigated and correlated to the NiMnGa functional properties. The material characterization was conducted by means of microstructural observation through optical and SEM microscopy, differential scanning calorimetry (DSC), mechanical analysis including strain recovery tests and dynamic mechanical thermal analysis (DMTA) for the damping characterization, X-ray diffraction analysis and electrical resistivity measurements. In this way, the physical characterization of the NiMnGa sintered alloy allowed a complete investigation of the evolution of the thermoelastic martensitic transition (TMT) and a correlation between thermomechanical condition and functional properties was possible. Moreover, magnetic measurements provided a preliminary characterization of the magnetic transition of the alloy and the effects of the sintering process on the magnetic properties were observed. This experimental study could be the starting point for the implementation of an alternative production method for NiMnGa alloy and for the optimization of the coupling between structural and magnetic order thanks to the combination of the functional and magnetic transitions.

Keywords: ferromagnetic shape memory alloys, NiMnGa, sintering, physical characterization, thermoelastic martensitic transition, magnetic properties

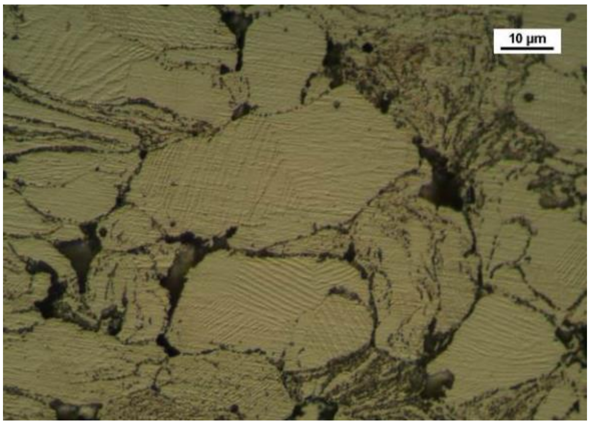


Figure 1: Martensitic structure of the $Ni_{50}Mn_{30}Ga_{20}$ alloy produced by ODP process and subjected to thermal treatment (925 °C for 6 hours)

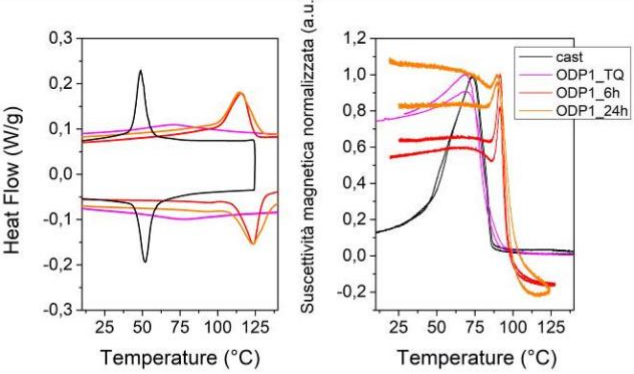


Figure 2: The effect of the ODP sintering process and thermal treatments on the functional and magnetic properties of NiMnG (DSC

analysis and magnetic susceptibility measurements)

References:

1. Sozinov, A., Likhachev, A. A., Lanska, N., and Ullakko, K. (2002) *Appl. Phys. Lett. 80*(10), 1746-1748.
2. Besseghini, S., Pasquale, M., Passaretti, F., Sciacca, A., Villa, E. (2001) *Scr. Mater.* 44, 2681–2687.
3. Dunand, D.C., Müllner, P. (2011) *Adv. Mater.* 23, 216–232.
4. Mostafaei, A., De Vecchis, P.R., Stevens, E.L. Chmielus, M. (2018) *Acta Mater.* 154, 355–364.

Elastocaloric properties of polycrystalline samples of NiMnGaCu ferromagnetic shape memory alloy in compression configuration

E. Villa[1], C. Tomasi[2], F. Villa[1], E. Bestetti[1], A. Nespoli[1], F. Passaretti[1]

[1] Consiglio Nazionale delle Ricerche – Istituto della Materia Condensata e di Tecnologie per l'Energia (CNR-ICMATE Sede di Lecco) via G. Previati 1/e, 23900 Lecco (Italy)
[2] Consiglio Nazionale delle Ricerche – Istituto della Materia Condensata e di Tecnologie per l'Energia (CNR-ICMATE Sede di Genova) Area della Ricerca di Genova, Via De Marini n°6, 16149 Genova (Italy)

Abstract:

Recently the SMA and FeSMA alloys have attracted interest for solid state refrigeration applications. Among NiMnGa-based quaternary systems, NiMnGaCu exhibits an interesting giant magnetocaloric effect thanks to the temperature overlapping of magnetic transition and thermoelastic martensitic transformation (TMT), in particular for compositions with about 6at% Cu content. In the present work in polycrystalline alloy samples with Ni50Mn18.5Cu6.5Ga25 at% chemical composition, we investigate the contribution of TMT to the total ΔS change in the elastocaloric performances, to give a functional characterization of effect of microstructure on caloric properties and to give information about perspective for magneto-mechanical coupling. We present an extensive calorimetric and thermo-mechanical characterization in compression configuration to explore the correlation between microstructural properties induced by means of selected thermal treatments and elastocaloric response. Our results give important hints on how the efficiency of the martensitic transition and its modulation in temperature has a final effect on the total ΔS measured.

Keywords: Ferromagnetic Shape Memory Alloys, Elastocaloric effect, Thermo-mechanical process

Figure 1: Martensite structure of NiMnGaCu sample.

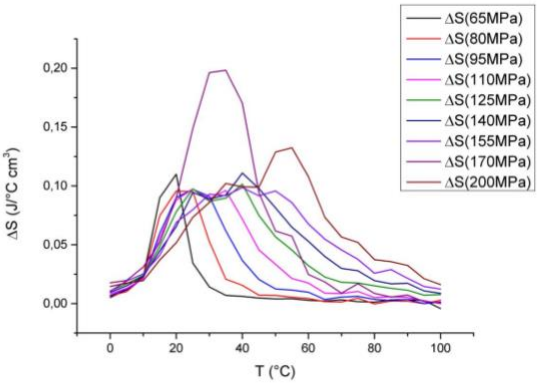


Figure 2: ΔS measures for elastocaloric properties

References:

1. E. Villa, C. Tomasi, A. Nespoli, F. Passaretti, G. Lamura, F. Canepa, (2020), *J. Mater. Res. Technol. 9(2), 2259–2266*
2. Sarkar SK, Sarita, Babu PD, Biswas A, Siruguri V, Krishnan M. (2016), *J Alloys Compd;670:281–288*

Magnetic and Dielectric Properties of Ruddlesden–Popper $Ca_3Mn_2O_7$ thin films prepared by Pulsed Laser Ablation

B. Silva [1*], J. Oliveira[1], T. Rebelo[1,3], P. Rocha-Rodrigues[2], N. Lekshmi[2],
A. Lopes[2], J. Araújo[2], L. Francis[3], B. Almeida[1]

[1] CF-UM-UP, Centro de Física da Universidade do Minho e da Universidade do Porto, Universidade do Minho, Braga, Portugal,
[2] IFIMUP, Institute of Physics for Advanced Materials, Nanotechnology and Photonics, Universidade do Porto, Porto, Portugal.
[3] INL, International Iberian Nanotechnology Laboratory, Braga, Portugal.

Abstract:

Naturally Layered Perovskite structures with improper ferroelectricity [1, 2], such as the Ruddlesden-Popper calcium manganite compound $Ca_3Mn_2O_7$, offer an alternative route to achieve non-expensive and high-performance room temperature multiferroic magnetoelectricity for information storage, sensors, and actuators or low power energy-efficient electronics. They allow exploring oxygen octahedra nonpolar rotations and cation site displacement to attain non-centrosymmetry. Additionally, due to their high sensitivity to lattice-distortions, their preparation in thin film form over crystalline substrates allows the manipulation of acentricity and enables the tuning of lattice, electric and magnetic interactions. However, the preparation conditions to obtain the $Ca_3Mn_2O_7$ phase with the Ruddlesden-Popper structure need to be optimized and their properties have not yet been explored. As such, thin films of $Ca_3Mn_2O_7$ have been prepared over $SrTiO_3$ substrates by Pulsed Laser Ablation, using a $Ca_3Mn_2O_7$ target. Polycrystalline $Ca_3Mn_2O_7$ was synthesized using a conventional high-temperature ceramic route. The structural studies show that in the films prepared on $SrTiO_3$, at 730 ºC, with 4 J/cm^2 laser fluence, 10^{-3} mbar oxygen pressure and with a post-annealing process, the $Ca_2Mn_3O_7$ phase is stabilized, as confirmed by XRD and Raman Spectroscopy. The corresponding EDS analysis further gives a Ca/Mn atomic ratio of ~1.5:1, consistent with the presence of this phase. The magnetic properties were measured using a SQUID magnetometer, showing an antiferromagnetic transition at 110 K. The dielectric properties of the films show a relaxor-type behaviour (fig. 1), described by the Vogel-Fulcher-Tammann equation. The dielectric and magnetic properties of the films will be discussed and presented, highlighting the phase evolution and stabilization in the films.

Keywords: Naturally Layered Perovskites, Ruddlesdon-Popper, Calcium manganite, Thin films, Laser Ablation, Structural properties, Morphology, Magnetic Properties, Dielectric Properties

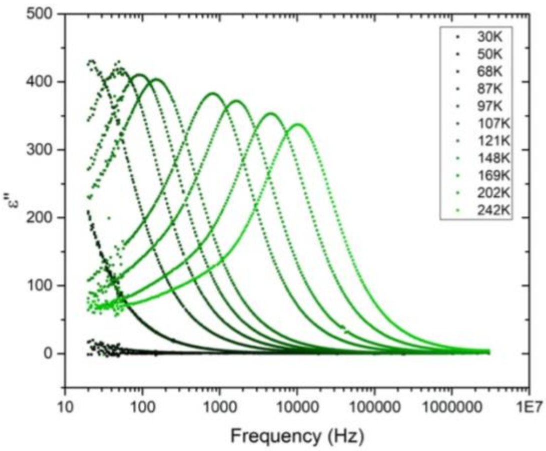


Figure 1: Imaginary permittivity in function of frequency for $Ca_3Mn_2O_7$ thin film prepared by Pulsed Laser Ablation.

References:

1. Ghosez, P., Triscone, J.-M., (2011). Coupling of three lattice instabilities: Multiferroics. Nature Materials, vol. 10, n. 4, 269–270.
2. Rocha-Rodrigues, P., Santos, S. S. M., Miranda, I. P., Oliveira, G. N. P, Correia, J. G., Assali, L. V. C., Petrilli, H. M., Araújo, J. P., Lopes, A. M. L., (2020). Ca3Mn2O7 structural path unraveled by atomic-scale properties: A combined experimental and ab initio study. Physical Review B, 101, 064103.

Analysis of Changes of Wood Color, Mass, Density and Total phenolic compounds after thermal treatment process

M. Aleinikovas [1,*], B. Šilinskas [1,] M. Škėma [1,]
I. Varnagirytė-Kabašinskienė [1,] L. Beniušienė [1,]

[1] Institute of Forestry, Lithuanian Research Centre for Agriculture and Forestry (LAMMC),

Kaunas, Lithuania

Abstract:

Wood, chemically described as a polymeric composite of cellulose, hemicellulose and lignin, is an economically important renewable resource that is widely used as an environmentally friendly material with properties suitable for industry and the private sector. Among many positive natural wood properties, producers of wood products or construction professionals find the wood properties that need to be improved. For example, wood biodegradability, dimensional non-stability under varying moisture contents, and degradability by ultraviolet (UV) light often limit the use of natural wood and its products. When wood is exposed outdoors, the photooxidation or photochemical degradation process begins: the color changes followed by the loss of fibers and surfaces erosion are often observed (Ayadi et al. 2003; Williams 2005; Garcia et al 2014). The wood properties change due to internal chemical reactions, and wood strength is lost as it biologically degrade due to oxidation, hydrolysis, and dehydration reactions (Rowell 1983, 2006).

Earlier studies indicated that that heat treatments cause colour stability of the wood when exposed to UV radiation, higher durability and dimensional stability to the wood (Vernois 2001; Garcia et al. 2014).

Wood specimens of five wood species (Pinus sylvestris L., Picea abies (L.) H. Karst., Pseudotsuga menziesii, Juglans Regia L. and Acer platanoides L.) were hydrothermally treated with the modifying solvents, containing different additives, as Fe_2O_3 or $FeCl_3$ with and without commercial tannins. This study aimed to identify the changes in wood of different tree species: the changes of mass and density; the changes in the content of total phenolic compounds in the solvents remained after thermal treatment process; and Fe concentration in wood.

This study has shown that wood response to different treatments after thermal processing were much dependent on tree species, therefore, different treatments had quite contradictory impact. Comparable response was obtained for two conifers – *Pinus sylvestris* and *Picea abies* – in case of mass loss and wood density. The treatments with additives Fe_2O_3 or $FeCl_3$ with and without commercial tannins increased the content of total phenolic compounds in the solvents compared with the control treatments.

Keywords: iron oxides, iron salt, commercial tannins, total phenolic compounds, mass loss, wood density, color change.

Figure 1: Norway spruce (*Picea abies*) after different treatment.

References:

1. Ayadi, N.; Lejeune, F.; Charrier, F.; Charrier, B.; Merlin, A. 2003. Color stability of heat-treated wood during artificial weathering. *Holz als Roh und Werkstoff* 61: 221-226.
2. Garcia, R.A., Lopes, J.D., Nascimento, A., & Latorraca, J.V. (2014). Color stability of weathered heat-treated teak wood. *Maderas-ciencia Y Tecnologia, 16*, 453-462.
3. Rowell RM (1983) Chemical modification of wood: A review. Commonwealth Forestry Bureau, Oxford, England, 6: 363-382.
4. Rowell RM (2006) Chemical modification of wood: A short review. Wood Material Science and Engineering 1: 29-33.

5. Vernois, M. 2001. Heat treatment of wood in France: state of the art. In: Rapp AO Review on heat treatments of wood. In: Special seminar: environmental optimization of wood protection, Antibes, France, 68 p.

6. Williams, R.S. 2005. Weathering of wood. In: *Rowell, R.M. (ed) Handbook of wood chemistry and wood composites.* CRC Press, Florida, pp. 139-185.

Emergent Opto-Electronic Properties in Molecular-Metal Polymer Nanocomposites

Raphael Pfattner, Elena Laukhina, Marta Mas-Torrent, Vladimir Laukhin, Concepció Rovira and Jaume Veciana

Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC) Campus UAB, 08193 Bellaterra (Spain)
and Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN)
ICMAB-CSIC, 08193 Bellaterra (Spain)
(*email address: rpfattner@icmab.es)

Abstract:
Developing smart materials that can respond to an external stimulus is of major interest in artificial sensing devices able to read information about the physical, chemical and/or biological changes produced in our environment. Additionally, if these materials can be deposited or integrated on flexible, transparent substrates, their appeal is greatly increased.

The first [BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene based quasi-twodimensional organic superconductor β-$(BEDT\text{-}TTF)_2I_3$ was first reported back in 1984.[1] Soon it became clear that ion radical salts (IRSs) derived from BEDT-TTF exhibit tuneable electronic band structures; therefore, such molecules are excellent building blocks for engineering a rich and diverse family of organic crystalline metals and semiconductors. Thanks to strong electron−electron and electron−phonon couplings, their anisotropic electronic structures exhibit many fascinating electronic and structural phase transitions, which can be controlled by external stimuli such as light, temperature, strain, pressure, and humidity, among others. Nevertheless, it is necessary to engineer these crystals into a proper material for sensing applications. This is done by forming polycrystalline layers of IRSs, derived from BEDTTTF-based conductors, in nanocomposite bilayer (BL) films.

Such systems can be further tuned by choosing the nature of the IRSs enabling high sensitivity towards strain, pressure, temperature or even contactless radiation sensing *i.e.* bolometers.[2,3] In another very recent example, bilayer films, composed of conducting polycrystalline layers of two dimensional BEDT-TTF-IRSs, hydroresistive sub-micron sized crystals on top of a polymeric host matrix permit to electrically monitor relative humidity in a stable and fully reversible fashion.[4] At the percolation threshold, fascinating novel optoelectronic properties emerge (Insulator semiconductor-like metal transition).[5] Mechanisms of responses are discussed and correlated with fundamental properties of charge transport in these systems. This sensor platform enables combining high electrical performance of single crystals with processing properties of polymers towards a simple, low-cost and highly sensitive platform for applications in robotics, biomedicine and human health care.

Keywords: Molecular conductors, tuneable opto-electronic properteies, metal insulator transition, human healthcare.

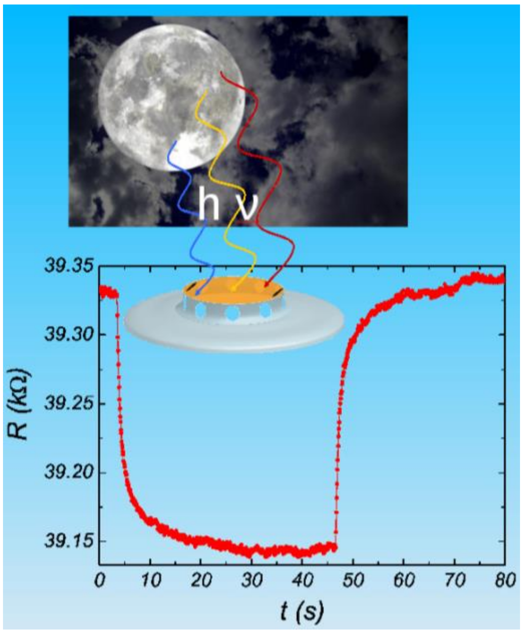


Figure 1: First reported full organic pyroresistive infrared bolometer[3].

References:

1. E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, et.al., JETP Lett., (1984), 39, 12.
2. E. Laukhina, R. Pfattner, L. R. Ferreras, et. al., Adv. Mater., (2009), 21, 1-5.
3. R. Pfattner, V. Lebedev, E. Laukhina, et.al., Adv. Electr. Mater., (2015), 1, 1500090.
4. R. Pfattner, E. Laukhina, L. Ferlauto, et.al, ACS Appl. Electr. Mater., (2019), 1, 1781.
5. R. Pfattner, et.al, (2021), submitted.

Multiply Positively Charged Cyclodextrin Derivatives Usable for Stable Modification of Negatively Charged Solid Support

J. Jindřich,* P. Kasal

Charles University, Faculty of Science, Department of Organic Chemistry, Prague, Czech Republic

Abstract

Ionic binding of modifiers to a solid support, which is a very convenient alternative to the covalent binding, was used, e.g., for preparation of Pirkle type chiral chromatographic columns[1]. Nevertheless, the low stability of the ionic bond in polar media represents a major limitation of its use.

Recently, we reported the use of doubly charged cyclodextrin (CD) derivatives as modifiers of the sulfonated silica gel for the preparation of the chiral column[2]. Although the stability of the column towards the polar media was better, the leakage of the modifier was still observable.

Here, we report the method for synthesis of a new type of multiply charged CD-based molecular anchors bearing from 7 to 24 positive charges – quaternary ammonium groups – concentrated to a small space using a neopentyl skeleton (which is also functioning as a stabilizer preventing Hofmann elimination). The anchors can be prepared from common chemicals without a need for chromatographic separations. The positive charges of the anchors are located at the primary side of the CD skeleton; the free hydroxyl groups located at the secondary CD side can be used for covalent attachment of the active compounds, e.g., by reaction with isocyanates (Figure 1).

The negatively charged solid support (cation exchange resin, zeolite, Nafion, silica gel, aluminum oxide, glass surface) can be modified by merely immersing it in an aqueous solution of the modifier. In this way, many materials used in practice can be prepared more readily, as demonstrated by the preparation of a modified silica gel solid-phase suitable for chromatographic separation, usable in a wide range of pH values.

Keywords: cyclodextrin derivatives, multiply positively charged derivatives, electrostatic binding, negatively charged solid support, silica gel, alumina, cation exchanger, zeolite, Nafion.

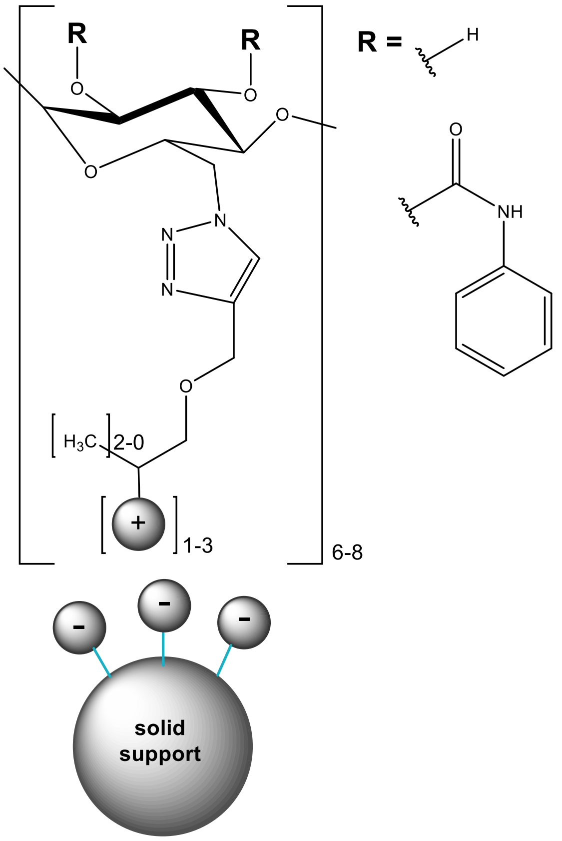


Figure 1: The structure of the cyclodextrin based multiply positively charged anchor/modifier strongly ionically bound to negatively charged solid support.

References:

1. Pirkle, W. H.; Finn, J. M. (1981) Chiral High-Pressure Liquid Chromatographic Stationary Phases. 3. General Resolution of Arylalkylcarbinols. *J. Org. Chem.* 46, 2935–2938.
2. Kučerová, G.; Kalíková, K.; Procházková, H.; Popr, M.; Jindřich, J.; Coufal, P.; Tesařová, E. (2016) Chromatographic Characterization of a New Cationic β-CD Based Stationary Phase Prepared by Dynamic Coating. *Chromatographia* 79, 529–536.

Microgels as “*on demand*” Cation Release Systems

V. Chimisso[1], S. Conti [1], P. Kong[1], C. Fodor[1], W. Meier[1]*

[1] Department of Chemistry, University of Basel, Basel, Switzerland

Abstract:

Metabolic diseases that involve the overaccumulation of metal cations in the body are nowdays treated with hormones, steroids and ion exchange resins.(1) In particular, ion exchange polymers, such as polystyrene sulfonate (commercially known as Kayexalate®) have very low efficiencies and can lead to harsh side effects in long term use, such as gut necrosis and ischemia.(1) In order to prevent these kind of side effects and increase the efficiency of the system, microgels could be potential candidates to act as ion scavengers without damaging the intestinal tract. These can be designed to be fully biocompatible whils bearing the chemical functionalities able to bind the targeted ion.(2)

Within this work, we present biocompatible vinylcaprolactam based microges (PVCL) containing itaconic acid, which with their inherently chelating structure, can reversibly bind divalent and trivalent cations.(3) Their behaviour towards a set of representative cations was tested, and the ions chosen were Mg^{2+}, Sr^{2+}, Cu^{2+} and Fe^{3+}. Their swelling in response to ions and pH changes was investigated via dynamic light scattering (DLS). The amount of ions bonded and released upon pH changes was quantifed with ion chromatography, also showing that for earth alkali ions, this process is fully reversible. We also demostrate how the system has a preferential binding affinity towards Fe^{3+} ions, making the microgels excellent candidates for biomedical applications which aim to fight iron overaccumulation diseases such as hemochromatosis.

Keywords: microgel, divalent and trivalent cations, reversible cation binding, cation selectivity.

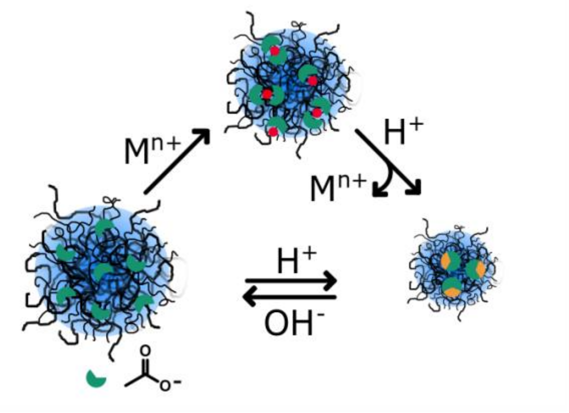


Figure 1: Figure illustrating microgels which can reversibly bind divalent and trivalent cations upon pH change.

References:

1. Palmer, B. F., & Clegg, D. J. (2017). Diagnosis and treatment of hyperkalemia. *Cleve Clin J Med*, *84*(12), 934-42.
2. Plamper, F. A., & Richtering, W. (2017). Functional microgels and microgel systems. *Accounts of chemical research*, *50*(2), 131-140.
3. Chimisso, V., Conti, S., Kong, P., Fodor, C., & Meier, W. P. (2021). Metal cation responsive anionic microgels: behaviour towards biologically relevant divalent and trivalent ions. *Soft Matter*, *17*(3), 715-723.

Smart polymer nanocomposites

I. Lorero[1], M. Campo[1], A. Jiménez-Suárez[1], S. G. Prolongo[1*]
[1] Materials Science and Engineering, University Rey Juan Carlos, Madrid, Spain

Abstract:

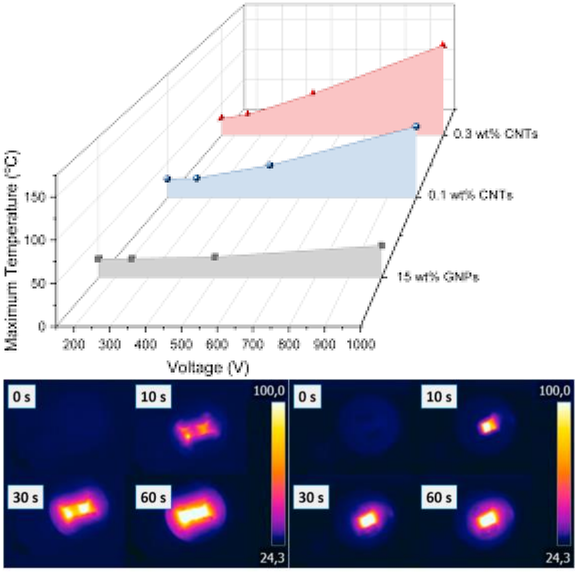
Smart polymers is being widely studied as new multifunctional materials able to interact intelligently with their environment. Shape memory (SM) and self-healing (SH) polymers are some of the most important ones. Their chemical nature can be different. In this work, we are centered on thermosetting polymers, which are usually used as matrix on composite materials. The most of the smart thermosetting polymers are switched by thermal stimulus. This means that the recovery of their shape (SM) or their structure (SH) is induced by an increment of temperature.

In order to wide their applicability, electrical conductor nanofillers are added to the smart thermosetting polymers. This allows becoming the thermal stimulus into an electrical imput, due to the resistive heating by Joule´s effect. These new smart composites are able to act, modifying their structure or shape, by application of electrical voltage with low energy comsuption. This allows a remote and easy control of the smart processes.

In this work, we introduce graphitic nanofillers, such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) into different smart thermosetting polymers. The minimum nanofiller content added is higher than its electrical percolation threshold. On the other hand, the polymers are shape memory and self-healing resins based on the incorporation of thermally reversible bonds, covalents or adducts. They present different chemical mechanisms to interact with the environment. We analyse the main thermal and mechanical behavior together with the SM and SH efficiency activated by convention or electrical resistive heating.

It is worthy to note that the electrical conductivity of the nanocomposites depends on the nature and geometry of conductor nanofiller, their dispersion on the matrix and even the electrical conductivy and the chemical interface with the insolating matrix. For this reason, the thermoelectrical properties will be analysed in order to optimized the resistivity heating with low consumption. On the other hand, the SM and SH process are be analysed, determining their efficiency as a function of the chemical nature of resins, particularly the reversible chemical bonds, and the mechanism of heating applied by convention or electrical resistivity.

Keywords: protein folding, nanoporous sol-gel glasses, silica-based biomaterials, circular dichroism spectroscopy, surface hydration, crowding effects, micropatterning, biomedical applications.



(a) (b)

Figure 1: Maximun temperature reached as a function of the geometry and added amount of graphitic nanofillers.

References:

1. Sánchez-Romate, X.F., Sans, A., Jiménez-Suárez, A., Prolongo, S.G. (2021) The addition of graphene nanoplatelets into epoxy/polycaprolactone composites for autonomous self-healing activation by Joule's heating effect, *Compos. Sci. Technol.* 213, 108950
2. Jiménez-Suárez, A., Martín-González, J., Sanchez-Romate, X.F., Prolongo, S.G. (2020) Carbon nanotubes to enable autonomous and volumetric self-heating in epoxy/polycaprolactone blends, *Compos. Sci. Technol*. 199, 108321
3. Doblas, A., Rosario, G.D., Prolongo M. G., Prolongo, S.G. Electric heating performance of nanodoped polyurethane coatings, *Progress in Organic Coating* 135, pp 185-190

Smart nanocomposites based on thermoset polymers reinforced with carbon nanostructures

A. Jiménez-Suárez [1*], V. Martínez-Martínez[1], M.I. Rodríguez-Tapiador[1], X.X.F. Sánchez-Romate[1], S.G. Prolongo[1]
[1] Materials Science and Engineering Area, Experimental Science and Technology School (ESCET), Universidad Rey Juan Carlos, Móstoles, Spain

Abstract:

Polymer nanoreinforced epoxy resins have attracted a great interest in the scientific community due to possibility of developing new polymer composites with new functionalities and low density.

Their use as coatings is widely extended over several substrates, i.e.: metallic, polymer, fiber reinforced composites, etc. Although protection/barrier and decorative are widely extended as purposes for these coatings, more specific technical functionalities, such as hydrophobic/hydrophilic, de-icing, self-sensing or self-heating, could be of great interest for many industries.

Their use in large structures with difficult accessibility, such as wind blades, has increased the interest on developing coatings with longer life in service, reduced preventive maintenance and the possibility of conferring new functionalities while keeping the traditional ones, which is usually referred as multifunctional coatings.

This research work explores two important aspects, the anti-icing and de-icing capabilities of these coatings and their capability to detect damage.

The addition of carbon nanostructures and thermoplastic phase in the epoxy resin has been proven in this work as an effective approach to increase reduce the wettability of the coatings by water, that is, improving their hydrophobic behavior which, in fact, should reduce the ice accretion on the surfaces. Different contents of carbon nanostructures and thermoplastic phase have been added to study the evolution of the wettability while keeping other basic thermal or mechanical properties.

The addition of carbon nanostructures in contents above the percolation threshold allow obtaining electrical conductive nanocomposites. This electrical pathways based on discontinuous networks of nanoreinforcements in contact, generate heat while a currents flow through them (Joule's effect heating). The research work proposes contents of carbon nanotubes (CNTs) and/or graphene nanoplatelets (GNPs) enough to reach temperatures that would allow de-icing at low power consumption. In fact, the content required for both types of nanoreinforcements is quite different although they have been tuned to reach the target of de-icing in both cases. Nevertheless, differences in surface quality were found when modifying the nanoparticle content, as the manufacturability changed. This aspect was very important as the wettability was affected by the surface quality and the carbon nanoparticle or thermoplastic content.

In order to improve the hydrophobic behavior of coatings, other nanofillers, such as graphene oxide (GO) and GO functionalized with F were also tested, proving a change in the behavior observed.

Finally, self-sensing capabilities by the creation of electrically conductive networks susceptible to strain and damage were tested. As previously demonstrated, sensitivity of the technique is improved when low contents (near the percolation threshold) are used [1], therefore, a balance between the self-heating capabilities and the self-sensing ones must be found for this type of materials. In fact, a multilayer coating with different capabilities can be proposed as a result of the study, depending of the functionality of the layer: hydrophobic, self-heating, self-sensing, leading to a multifunctional multilayer coating.

Keywords: coating, multifunctional materials, smart materials, carbon nanotubes, graphene nanoplatelets, nanocomposites, hydrophobic, thermal properties, self-sensing, structural health monitoring.

References:

1. Li B, Ma P, Cho W S et al. (2007) Correlations between Percolation Threshold, Dispersion State, and Aspect Ratio of Carbon Nanotubes, *Adv. Funct. Mater.*, 17, 3207-15

Electrical, thermo-electrical and electro-magnetical behaviour of graphitic nanofillers/epoxy nanocomposites

I. Collado[1], A. Jiménez-Suárez[1], G. Del Rosario[2], S. G. Prolongo[1*]
[1] Materials Science and Engineering, University Rey Juan Carlos, Madrid, Spain
[2] Technological Support Center, University Rey Juan Carlos, Madrid, Spain

Abstract:

Graphitic nanoparticles, such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs), are widely studied as nanofillers of polymer matrix in order to enhance their chemical and mechanical properties and, in addition, to change their electrical behavior. The nanocomposites are electrical conductors when the percentage of nanofillers is higher than their electrical percolation threshold. However, the formation of the electrical network strongly depends on the dispersion degree of the nanofillers, which depends, in turn, on the manufacturing process.

On the other hand, the relative low electrical conductivity of nanocomposites enables the resistivity heating by Joule´s effect. Again, the thermos-electrical properties also depends on the nature, geometry and dispersion degree of nanofillers. In addition, the insulated matrix affects to their thermos-electrical behavior, depending on the generated strong or weak interface and the own electrical conductivity of the resin.

Finally, it is well known that the reinforcement of the resins mofidies also their electromagnetical behavior. In particular, the geometry and nature of nanofillers modify the electromagnetic shielding of the nanocomposites.

In this work, we study the influence of the nature and geometry of nanofillers (CNTs, GNPs and magnetite), the added content and the dispersion degree on the electrical, thermoelectrical and electromagnetical behavior of the epoxy nanocomposites. In order to modify the dispersion degree of nanofillers different techniques and experimental procedures were applied, modying the time and amplitude of sonication and the number of calandering steps. Interesting relationships have been obtained between the studied properties and the structure of nanocomposites.

Keywords: Electrical properties, Thermoelectrical properties, Electromagnetic shielding, Nanocomposites.

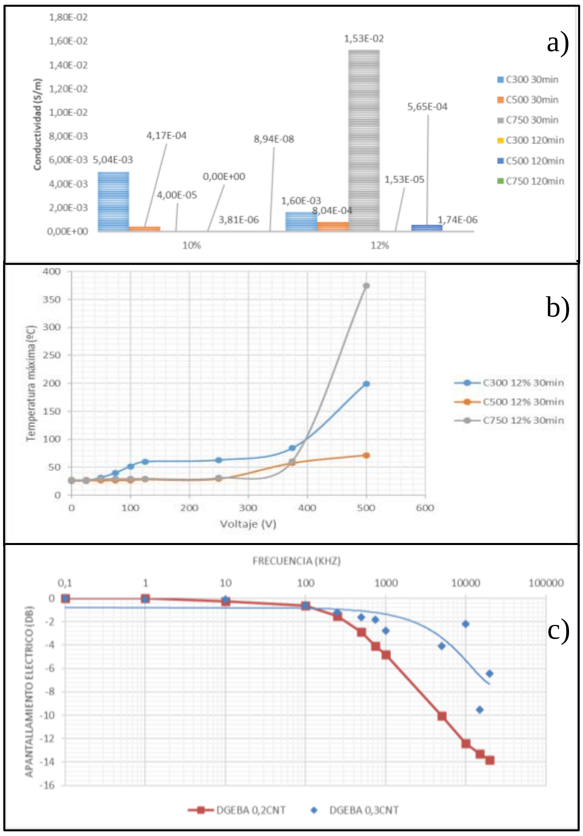


Figure 1: a) Electrical conductivity as a function of the applied sonication time on GNP/epoxy nanocomposites; b) Joule´s heating as a function of the applied voltage for different GNPs; and c) Electromagnetic shielding as a function of the CNT contents.

References:

1. Doblas, A., Rosario, G.D., Prolongo M. G., Prolongo, S.G. Electric heating performance of nanodoped polyurethane coatings, *Progress in Organic Coating* 135, pp 185-190
2. Sánchez-Romate X.F., Jiménez-Suárez, A., Campo M., Ureña, U., Prolongo, S.G. Electrical properties and strain sensing mechanisms in hybrid graphene nanoplatelet/carbon nanotube nanocomposites. Sensors 21 (16) 5530.

Smart Materials and Surfaces 2021 / Sensors 2021 Joint Onsite Session I

Advances in light activated gas sensors based on ZnO nanowires

G. Ambrosio[1], Thi Thanh Le Dang[3], D. Rocco[2], C.De Angelis[2,1], G. Faglia [2,1], and C. Baratto [1*]
[1] CNR-INO, PRISM Lab, Brescia, via Branze 45, Italy
[2] DII-University of Brescia, Via Branze 38, Italy
[3] ITIMS-Hanoi University of Science and Technology (HUST), Hanoi, Vietnam

Abstract:

Metal oxide semiconductors-based gas sensors have been extensively explored due to their high sensing response, cost-effectivity, long-term stability, and simple fabrication. Here we concentrate on ZnO, which is one of most important semiconductor materials for chemical sensing, thanks to its high surface reactivity towards explosive and toxic gases and ease of preparation in single crystalline nanostructures [1]. Due to almost monocrystalline perfection, nanowires (NWs) exhibit excellent thermal stability that makes them superior to polycrystalline thin-film sensor. Gas sensing is achieved by monitoring conductance variation of NWs at high temperature, but reduction in power consumption is highly essential for long-term usage of gas sensors [2]. In this work, we investigated the effect of light activation on the gas sensors based on aligned NWs. We tested the effect of sub and supra band-gap illumination on the sensing capabilities of nanowires. Light activated devices were found effective for NO_2 sensing, with no interference to ethanol and relative humidity.

A micro/nanostructured ZnO crystal generally has a wurtzite structure and usually presents a hexagonal cross-section, which naturally serves as a Whispering Gallery Mode (WGM) microcavity owing to its high reflective index. Based on the resonant process, another way to use ZnO as a chemical sensor is to to detect surface properties changes, as WGM performance is very sensitive to the surface refractive index [3]. Here we prepared and investigated WGM properties of ZnO microwires prepared by hydrothermal growth, excited with UV light.

Keywords: nanowire, optical activation, gas sensor, WGM.

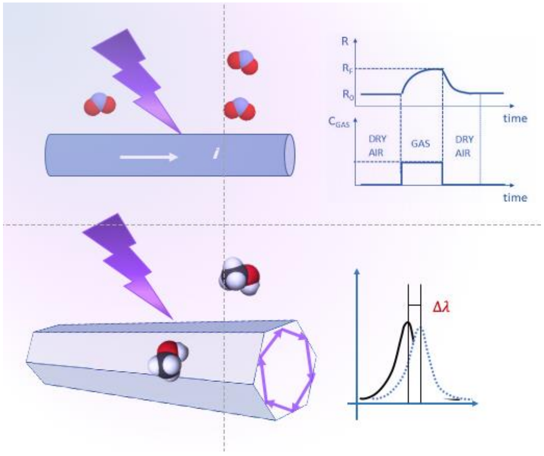


Figure 1: Figure illustrating the ZnO nano/microstructure and it application for ìgas sensing by different transduction methods: top) conductometric sensor with light activation; down) variation of the medium refractive index.

References:

1. C. Baratto, S. Todros, G. Faglia *et al.* (2009) "Luminescence response of ZnO nanowires to gas adsorption," *Sens.& Act. B,* 140, 2, 461-466, 2009.
2. C. Baratto, Viktoria Golovanov, G. Faglia *et al.* (2020) “On the alignment of ZnO nanowires by Langmuir – Blodgett technique for sensing application”, *Appl. Surf. Sci.*, 528, 146959
3. R. Chen, B. Ling, X. W. Sun *et al.* (2011) "Room Temperature Excitonic Whispering Gallery Mode Lasing from High-Quality Hexagonal ZnO Microdisks," *Adv. Mat.*, 23, 19, 2199-+.

Multi-functionalized silica nanoparticles to improve the sensitivity of diagnostic assays

C. Chaix [1*], C. Farre [1], M. Manzano [2], J. Vidic [3]

[1] Institut des Sciences Analytiques, Université de Lyon, CNRS/Université Claude Bernard Lyon 1, France.

[2] Dipartimento di Scienze AgroAlimentari, Ambientali e Animali, Università di Udine, Italy.

[3] Université Paris-Saclay, INRAE, AgroParisTech, Micalis Institute, Jouy-en-Josas, France.

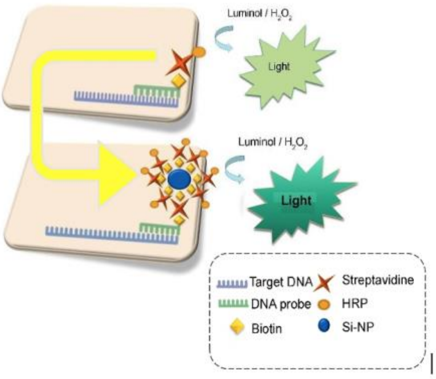
Abstract:

Silica nanoparticles (NPs) were functionalized by a solid-phase synthesis technology previously reported by our group.[1] The technology enables the development of highly functionalized and controlled nanomaterials of multiple properties. In the process, NPs are first immobilized on a controlled pore glass (CPG) support. The resulting assembled nano-on-micro (NOM) support is placed in a DNA/RNA synthesizer to perform NP functionalization *via* phosphoramidite chemistry.[1]

This technology was used for different applications. First, nanoparticle-based electrochemical sandwich immunoassay was developed for bacterial detection. For this, innovative methylene blue-DNA/nanoparticle assemblies were designed by exploiting the technology. This strategy ultimately produced highly functionalized nanoparticles with electrochemical markers. The methylene blue/DNA-NPs assemblies enabled amplification of the electrochemical signal x1000 compared to signal obtained without NPs. A limit of detection of 10 CFU/mL was achieved for *E. coli* bacteria in platelet concentrates.[2]

The second application of our technology concerned the development of a nanoparticle-based enzymatic immunoassay for Influenza A virus detection. Biotin and DNA functionalized NPs were developed. We succeeded to specifically detect Influenza A viruses (H1N1 and H3N2) directly in the lysis buffer supplemented with 10% saliva to simulate the clinical context.[3] The NPs based assay improved the sensitivity compared to the classical assay ELISA.

The third application concerned the development of a paper-based DNA dot blot sensor for *Campylobacter* detection.[4] Biotinylated silica-nanoparticles (biot-Si-NPs) were used to increase the sensitivity of detection. After immobilization of bacterial genomic DNA onto a paper membrane, and addition of a biotinylated-DNA detection probe, hybridization was evidenced using biot-Si-NPs and streptavidin conjugated to horseradish peroxidase (HRP) in the presence of luminol and H_2O_2. A limit of detection of 3 pg/µL of DNA was determined (600 CFU/mL). We demonstrated that the new dot blot coupled to Strepta/biot-Si-NPs successfully detected *Campylobacter* in naturally contaminated chicken meat, without needing a PCR preamplification.



Patent : BVT FR2005578-IT102020000012496

Fig. 1: Nanoparticle-enhanced DNA Dot Blot for *Campilobacter* spp. detection

Keywords: Si-nanoparticles, multi-functionalization, DNA dot blot, Multiplex bacterial detection, Influenza A dectection, Diagnostic assays.

References:

1. De Crozals G, Farre C, Hantier G, Léonard D, Marquette C, A., Mandon C, A., Marmuse L, Louis C, Toulmé J-J, Billotey C, Janier M, Chaix C. Oligonucleotide solid-phase synthesis on fluorescent nanoparticles grafted on controlled pore glass. *RSC Advances*, 2, 11858-11866 (2012)
2. Bonnet R, Farre C, Valera L, Vossier L, Léon F, Dagland T, Pouzet A, Jaffrézic-Renault N, Fareh J, Fournier-Wirth C, Chaix C. Highly labeled methylene blue-ds DNA silica nanoparticles for signal enhancement of immunoassays: Application to the sensitive detection of bacteria in human platelet concentrates. *Analyst*, 143(10), 2293-2303 (2018)
3. Farre C., Viezzi S., Wright A., Robin P., Lejal N., Manzano M., Vidic J., Chaix C., Specific and sensitive detection of Influenza A virus using a biotin-coated nanoparticle enhanced immunomagnetic assay, *Analytical Bioanalytical Chemistry*, (2020)
4. Vizzini P., Manzano M., Farre C., Meylheuc T., Chaix C., Ramarao, N., Vidic J., Highly Sensitive Detection of *Campylobacter spp.* in Chicken Meat using a Silica Nanoparticle Enhanced Dot Blot DNA Biosensor, *Biosensors and Bioelectronics*, 171, 112689 (2021)

Advanced technologies for Piezoelectric Sensors in SHM systems: a review.

L. Capineri [1]
[1] Department of Information Engineering, University of Florence, Florence, Italy

Abstract:
The scientific and technical challenges posed by the new era of space flights for the exploration of planets is one of the main drivers for advanced structural health monitoring (SHM) systems.

The main componenents of these systems and their interaction are reported in the illustration in Figure 1. This review is focused on the analysis of the state of the art of sensors for guided ultrasonic waves for the detection and localization of impacts. The recent developments in sensor technologies are then reported [1][2][3]. The physical phenomena that are related to impact event and the related main physical quantities are then introduced to discuss their importance in the development of the hardware and software components for SHM systems. In this context, the analysis of the front-end electronics is deepened, the type of data transmission both in terms of wired and wireless technology and of online and offline signal processing [4]. The integration aspects of sensors for the creation of networks with autonomous nodes with the possibility of powering through energy harvesting devices and the embedded processing capacity is also reported. Finally, the emerging sector of processing techniques using deep learning and artificial intelligence concludes the review by indicating the potential for the detection and autonomous characterization of the impacts and related damages.

Keywords: structural healthmonitoring (SHM); acoustic emission; guided waves; Lamb waves; sensors; ultrasound; piezoelectric; composites; piezopolymers; PVDF; interdigital transducer (IDT); PWAS; CMUT; mems; analog electronic front end; analog signal processing; impact localization; impact detection; sensor node; wireless sensor networks (WSN); IoT; deep learning; artificial intelligence.

References:

1. Mitra, M.; Gopalakrishnan, S. Guided Wave Based Structural Health Monitoring: A Review. Smart Mater. Struct. 2016, 25, 053001.
2. Giurgiutiu, V. Structural Health Monitoring with Piezoelectric Wafer Active Sensors, 2nd ed.; Academic Press, an Imprint of Elsevier: Amsterdam, The Netherlands, 2014; ISBN 978-0-12-418691-0.
3. Zhou, G.; Sim, L.M. Damage Detection and Assessment in Fibre-Reinforced Composite Structures with Embedded Fibre Optic, Sensors-Review. Smart Mater. Struct. 2002, 11, 925–939.
4. Capineri, L.; Bulletti, A. Ultrasonic Guided-Waves Sensors and Integrated Structural Health Monitoring Systems for Impact Detection and Localization: A Review. Sensors 2021, 21, 2929. https://doi.org/10.3390/s21092929

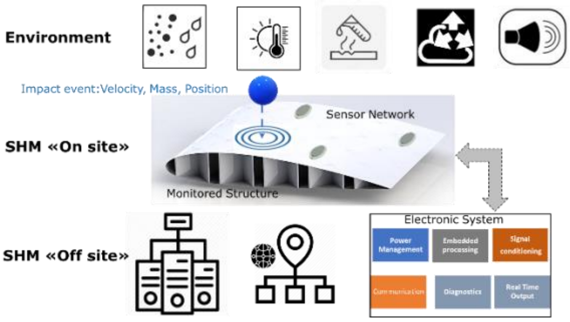


Figure 1: Illustration of the main componenents of an advanced structural health monitoring (SHM) system for impact monitoring. (Top) Environmental conditions (dust, moisture, temperature, pressure, vibrations, electromagnetic interference) and impact events characterized by the object mass, velocity, shape and dimensions. (Centre) On-site components of the SHM system subjected to environment conditions installed on the monitored structure (e.g., a section of a composite airplane wing). (Bottom) Off-site components installed remotely and connected to the sensors network; the Electronic System can operate in a protected environment (e.g., inside airplane fuselage) with real-time processing capability. Off-line signal/data processing based on big data archive with workstations connected to the web for software applications of Artificial Intelligence/Machine Learning (AI/ML) and prognostics.

Molecularly Imprinted Polymer Capacitive Chemosensor for Determination of Heterocyclic Aromatic Amines

Viknasvarri Ayerdurai[1], A. Garcia-Cruz[1], Maciej Cieplak[1,*], Piyush Sindhu Sharma[1],
Francis D`Souza[2,*], and Wlodzimierz Kutner[1,3,*]
[1] Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS),
Kasprzaka 44/52, 01-224 Warsaw, Poland
[2] Department of Chemistry, University of North Texas,
1155 Union Circle, #305070, Denton, TX 76203-5017, USA
[3] Faculty of Mathematics and Natural Sciences, School of Sciences,
Cardinal Stefan Wyszynski University in Warsaw,
Woycickiego 1/3, 01-815 Warsaw, Poland

Abstract:

Quinoxaline heterocyclic aromatic amines (HAAs) are formed during meat and fish cooking, frying, or grilling at high temperatures.[1] HAAs are classified as potent hazardous carcinogens, even though the HAAs are usually generated at very low concentrations (~ng per g of a food sample). This is because the HAA food contaminants effectively damage DNA by intercalation or strand break.[2] Hence, chronic exposure to HAAs, even in low doses, can cause cancers of the lung, stomach, breast, etc. Currently, HPLC is used for the determination of these toxins in food matrices.[3] However, this technique is expensive, tedious, and time-consuming. Therefore, fast, simple, inexpensive, and reliable HAAs determination procedures, without the need for separation of these toxins, in the protein food matrices are in demand. Molecularly imprinted polymers (MIPs) are excellent examples of bio-mimicking recognition materials. Therefore, they have found numerous applications in selective chemosensing. Within the present project, we synthesized a nucleobase-functionalized molecularly imprinted polymer (MIP) as the recognition unit of an electrochemical chemosensor for selective capacitive (Figure 1) detection and determination of 2-amino-3,7,8-trimethyl-3*H*-imidazo[4,5-*f*]quinoxaline (7,8-DiMeIQx) HAA. MIP-(7,8-DiMeIQx) film-coated electrodes were sensitive and selective to 7,8-DiMeIQx. The linear dynamic concentration range of the devised chemosensor extended from 47 to 400 µM 7,8-DiMeIQx, and the imprinting factor was high, IF = 8.5.

Keywords: Heterocyclic aromatic amine, quinoxaline, impedimetric chemosensor, molecularly imprinted polymer, nucleobase bithiophene derivative, intercalation, allosteric recognition, molecular recognition, bio-mimicking material.

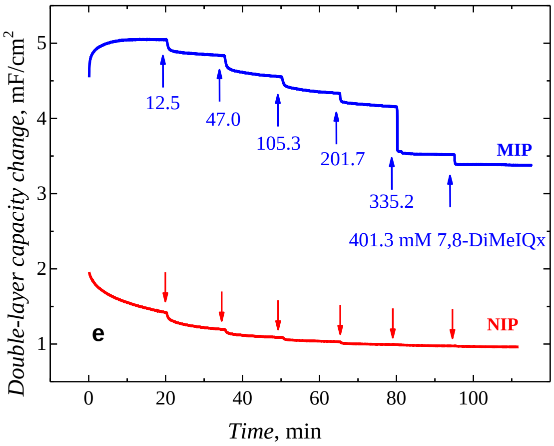


Figure 1: Capacity changes with time for the MIP and non-imprinted polymer (NIP) film-coated Au disk electrodes after the addition of 7,8-DiMeIQx of different concentrations.

References:

1. Gibis, M. (2016), Heterocyclic Aromatic Amines in Cooked Meat Products: Causes, Formation, Occurrence, and Risk Assessment, *Compr. Rev. Food Sci. Food Saf.*, 15 (2), 269-302.
2. Boer, D. R. (2009), Canals, A.; Coll, M., DNA-binding drugs caught in action: the latest 3D pictures of drug-DNA complexes, *Dalton Trans.*, 3, 399-414.
3. Barzegar, F.; Kamankesh, M.; Mohammadi, A. (2019), Heterocyclic aromatic amines in cooked food: A review on formation, health risk-toxicology and their analytical techniques, *Food Chem.*, 280, 240-254.

Challenges for a High Temperature Glass Solder for the Assembly Concept of a Piezoelectric Resonator

F. Kohler [1], M. Schulz [2], H. Fritze [2], J. Wilde [1]

[1] University of Freiburg – IMTEK, Department of Microsystems Engineering, Freiburg, Germany
[2] Clausthal University of Technology, Institute of Energy Research and Physical Technologies, Goslar, Germany

Abstract:

Implementing sensors that have a high sensitivity and a low measurement uncertainty at temperatures up to 1000 °C is a great chal-lenge. Therefore, the enclosure plays a decisive role in this temperature range. In this assembly concept for a sensor up to 1000 °C, glass solders provide the connection between the ceramic components of the housing (figure 1).

The Resonator is a bulk acoustic wave (BAW) sensor. The propagation of the acoustic waves occurs in the 300 µm thick substrate. The sensor material represents $Ca_3TaGa_3Si_2O_{14}$ (CTGS) as a piezoelectric single crystal. With a melting point of 1370 °C, CTGS shows sufficient temperature stability. The body oscillation frequency and the displacement change with temperature, which allows a sensor signal to be generated. The resonator has a keyhole-shaped platinum electrode on the top and bottom sides applied by thin-film metallization.

Various requirements are placed on this connection. On the one hand, it should have low conductivity even at high temperatures, since a metal feed-through of the sensor contacts through this material is planned. Furthermore, the coefficient of thermal expansion must be adapted to the structural elements to avoid high thermal-mechanical stress. Another point is the hermeticity. The glass solder connection represents a component of the encapsulation of the sensor to the outside. Therefore, it should be hermetically tight to protect the sensitive sensor from harsh environmental conditions.

Therefore, conductivity measurements on glass solder samples are performed in this work. Furthermore, the thermal expansion coefficient of the material itself is characterized as well as the expansion in connection with the housing components. The hermeticity is determined by helium leakage tests based on complete sensor housings.

Through the presented investigations, functional sensors could be built according to this concept.

Keywords: high temperature sensors, glass solder, ceramic conductivity, coefficient of thermal expansion, hermeticity of the package.

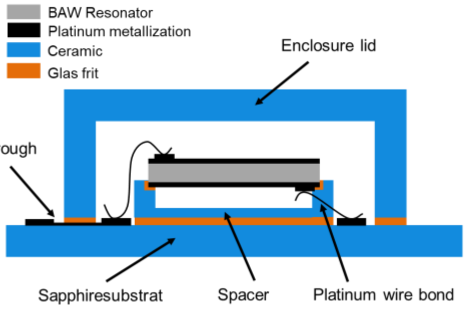


Figure 1: Figure illustrating the structural concept of the sensor package. The metal feedthrough and the glass solder applied to it can be observed. The hermeticity of the housing can be realized by a leakage-free connection through glass solder of the housing cap.

References:

1. Fritze, H. (2011) High-temperature piezoelectric crystals and devices, *J. Eletrocera-mics 26*, pp. 122-161.
2. Schulz, M., Kohler, F., Wilde, J., Fritze, H. (2021) Housed Temperature Sensors Based on Piezoelectric Resonators for High-Temperature Applications, *Sensor and Measurement Science International.*
3. Kohler, F., Farina, M., Zeitouny, Z. Schulz, M., Fritze, H., Wilde, J. (2021) Materialien und Prozesse für zuverlässige Aufbautechnologien von piezo-elektrischen Sensorelementen bis 1000 °C, *4. Symposium Materialtechnik des Clausthaler Zentrum für Materialtechnik.*

Metal nanoparticules decorated graphene for the developpement of gas sensors dedicated to sulfur-containing pollutants

E. Ruiz [1], T. Gueye [1], C. Varenne [1], A. Ndiaye [1], J. Brunet [1] A. Pauly [1]

[1] Université Clermont Auvergne, CNRS, Sigma Clermont, Institut Pascal, F-63000 ClermontFerrand, France

Abstract:

Graphene is a two-dimensional material with a high surface area and exceptional electrical properties[1]. Thanks to its properties this material is used in a wide range of applications, including energy-related fields, water purification, optical devices, field effect transistors, chemical and biological sensors, etc. However for electronic applications, such as resistive sensors, graphene is limited due to its zero band-gap[1]. One solution is to oxidize the graphene to open or tune the gap. Furthermore, the generation of oxygenated groups through oxidation allows to create actives sites for resistive gas sensors. But depending on the rate of oxidation, graphene oxide (GO) can become too resistive, and therefore less interesting for our purpose. For this reason, reduction processes are used to limit the oxidation rate. In fact, the GO reduction allows the preparation of reduce graphene oxide (RGO) with electronic properties that are useful for application in the field of sensors for example. This reduction process works as the removal of a part of the oxygen containing functional groups, allowing a less resistive material. The reduction can be achieved by several methods, chemical, thermal, electrochemical, with microorganisms or photoreduction[2]. Graphene-based materials and its derivatives are already used for the detection of various gas species. Due to its defects and functional groups, RGO prepared chemically or physically, seems to be a good candidate for gas sensing applications. Furthermore, the decoration by metallic nanoparticles allow to target toxic gases such as H_2S and SO_2, by creating specific interactions with these gases. Additionally, this decoration seems to be a key point to solve the sensor selectivity probem inherent to all sensors.

Here we prepared reduced graphene oxide by chemical reduction using a reducing agent. Then the RGO is decorated with metallic nanoparticles (Au, Pt, Cu, Pd) by chemical and physical routes and deposited by drop casting on interdigitated electrodes. After the caracterization of these layers, we will discuss the sensing performance and sensing mechanism, doping-efficiency, the behavior of the RGO without decoration and results at H_2S exposition at room temperature and high temperature. Specific behavior related to n-p transition (figure 1) for RGO has been highlighted and its origin will be discussed in details.

Keywords: graphene oxide, graphene, gas sensors, H_2S, SO_2, reduced graphene oxide, resistive sensors, metal decoration.

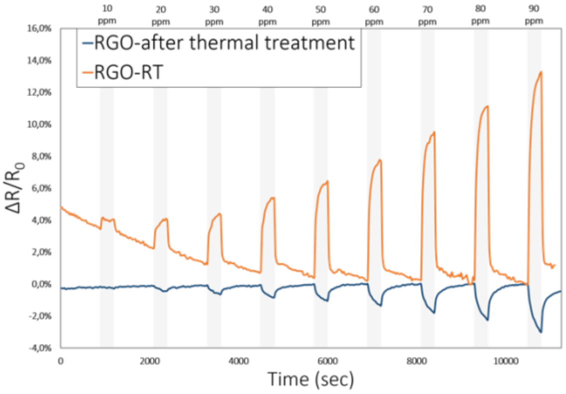


Figure 1: Exposure of RGO to H_2S at room temperature and after heat treatment clearly highlighting the n-p transition of the RGO caused by the thermal treatment.

References:

1. Castro Neto, A. H., Guinea, F., Peres, N. M. R., Novoselov, K. S. & Geim, A. K. The electronic properties of graphene. *Rev. Mod. Phys.* **81**, 109–162 (2009).
2. Agarwal, V. & Zetterlund, P. B. Strategies for reduction of graphene oxide – A comprehensive review. *Chem. Eng. J.* **405**, 127018 (2021).

Ultra hight sensitive NO_2 gas microsensor for environmental monitoring or mapping urban air quality

T. Gueye [1*], J. Brunet [1], A. Ndiaye [1] C. Varenne [1], E. Ruiz [1], A. Pauly [1]
(1) Université Clermont Auvergne, CNRS, Institut Pascal, F-63000 CLERMONT-FERRAND, FRANCE

Abstract:

Nitrogen dioxide is one of gaseous air pollutants produced from natural sources, motor vehicles, and other fuel-burning processes. Exposure to NO_2 can cause impairment for humans health, are harmful to plants and its presence into the troposphere contributes to the formation and modification of other air pollutants. Risks caused by continuous exposures at low concentrations of NO_2 are poorly characterized [1]. Due to its toxicity for human and environnement even at low concentrations, it's imperative to ensure a continuous monitoring of this gas in atmosphere. In order to carry out a high-resolution mapping of the air quality in an urban environment [2], the development of low-cost gas microsensors enable to measure the NO_2 concentration below its critical concentration with high sensitivity is highly needed. Because of its peculiar reactivity with oxidizing species and its unsensitivity with reducing ones, copper phthalocyanine (CuPc) is an organic molecular material that has been widely employed for the detection of oxidizing pollutants especially NO_2. This lecture deals with the sensing potentialities of nanometric layers (thickness <100nm) associated to conductimteric transduction for nitrogen dioxide monitoring in air. Our investigations focused on the study of CuPc thin films with thickness in the 50-100 nm range. Intercomparison of sensor sensitivity reveals that best results are obtained with 100 nm of thickness.

Gas sensor characterization under pollutant highlight a very sensitive, repeatable and reproducible NO_2 gas sensor with a very low detection limit of 4 ppb at 60°C. Such microsensor can be used for high resolution air quality mapping in an urban environment. It can also be used in an early detection system for NO_2 before the critical concentration. The effects of humidity and other interfering air pollutants (H_2S, SO_2, O_3 and COVs) on the sensor response have been investigated. A high level of selectivity was reached. Measurements towards NO_2 performed in wet atmospheres reveal that the presence of water vapor increases the sensor response. It constitutes a great advantage for sensors aimed to be distributed in real environnement.

Keywords: Phthalocyanine, Nitrogen dioxide, Gas microsensor, Gas monitoring, humidity effects.

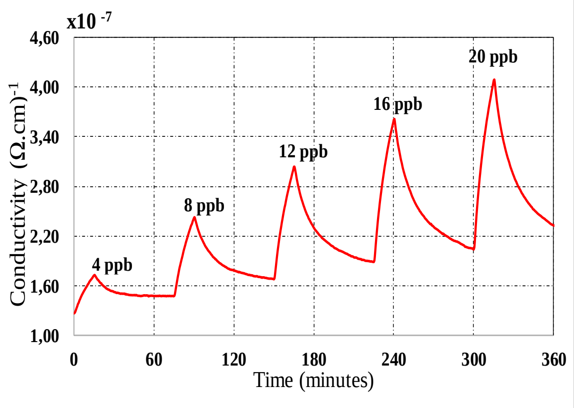


Fig 1: Electrical conductivity variations of 50nm CuPc layer thickness sequentially exposed to different concentration of nitrogen dioxide into the 4 - 20 ppb concentration range during 15min and to zero air during 60min.

References:

1. Tee Lamont Guidotti (1978). The higher oxides of nitrogen: Inhalation toxicology. , 15(3), 0–472. doi:10.1016/0013-9351(78)90125-1
2. Schneider, Philipp et al., (2017). Mapping urban air quality in near real-time using observations from low-cost sensors and model information. Environment International, (2017), S0160412016310741–doi:10.1016/j.e vint.2017.05.005

Transmissibility estimation of a metamaterial-based decoupling device for vibration measurement

A. Annessi[1,*], P. Chiariotti[2], V. Zega[3], M.Martarelli[1], P.Castellini[1]
[1] Department of Industrial Engineering and Mathematical Sciences, Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona, Italy
[2] Department of Mechanical Engineering, Politecnico di Milano, Via La Masa 1, 20156 Milano, Italy
[3]Department of Civil and Environmental Engineering, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20133 Milano, Italy

Abstract:

Vibrational measurements are a landmark in structural dynamics. This is true also for fault diagnosis and product quality assessment. These measurements are usually performed using piezoelectric accelerometers attached to the structure under investigation. The connection is usually made using adhesive or beeswax, magnets or threaded pins. However, the process of installing these sensors can be time-consuming and, in some cases, irreversible or even not-allowed. Hand-held vibration probes were widely used in the past, even though their performances (analysis band and overall accuracy) were lower compared to fixed installations. However, the spread of robots and the advancement in electronics caused a new interest in this solution. The handle design is crucial to ensure constant contact between the accelerometer and the target structure being tested. Furthermore, spurious vibrations, due to the handling by a human operator or a robot, need to be avoided introducing a decoupling element. Instead of using conventional materials, like rubber, this papers aims at presenting a decoupling element that exploits a metastructure. Its design is based on a periodic repetition of unit cells characterized by a strong mode separation and, thus, a wide frequency bandgap, i.e. frequency range where wave propagation is not allowed [1]. The decoupling element is built by joining more unit cells together. A repetition of three unit cells is chosen as the best compromise between amplitude reduction in the frequency band of interest and structure slenderness. Figure 1-a shows the decoupling element made of three unit cells realized by additive manufacturing in Nylon PA2200. It is connected to the shaker and the two accelerometers attached on the vibrationg base (input accelerometer) and on the free end of the element (output accelerometer). The vibration transmissibility of the element has been experimentally evaluated by measuring the ratio between the acceleration at the two sides of the element when it was forced into vibration by an electrodynamic shaker. The estimated transmissibility (i.e. the decoupling performance of the metastructure) is illustrated in Figure 1-b. It is evident that the vibration transmission above 1 kHz is completely hampered, being the transmissibility below 0.01.

Keywords: metamaterial, additive manufacturing, vibration isolation, transmissibility measurement

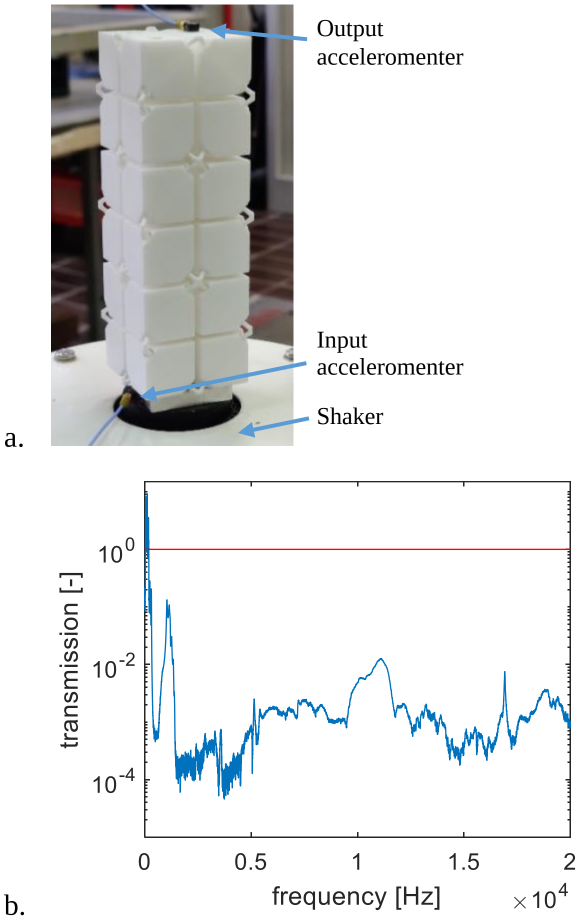


Figure 1: The geometry of the metamaterial decoupling element (a), and transmission diagram (b).

References:

1. D'Alessandro, L.; Belloni, E.; Ardito, R.; Braghin, F.; Corigliano, A. Mechanical Low-Frequency Filter via Modes Separation in 3D Periodic Structures. *Appl. Phys. Lett.* **2017**, *111*, 231902, doi:10.1063/1.4995554.

Transdermal Monitoring of Total Catecholamine via a Microneedles-based Nanoporous Gold Electrochemical Sensor

C. Tortolini[1], M.A. Venneri[1], A.E.G. Cass[2], A. Lenzi[1], R. Antiochia[3,*]
[1]Department of Experimental Medicine, Sapienza University of Rome, Rome, Italy
[2]Department of Chemistry & Institute of Biomedical Engineering, Imperial College, London, UK
[3]Department of Chemistry and Drug Technologies, Sapienza University of Rome, Rome, Italy

Abstract:
Microneedles arrays for minimally invasive continuous sensing in the dermal interstitial fluid (ISF) have been demonstrated in both amperometric [1,2] and potentiometric [3] modes for detection of several biomarkers of clinical interest [4], however there are no publication where microneedle arrays have been used for direct monitoring of total catecholamines in ISF.

Dopamine (DA), epinephrine (EP) and norepinephrine (NEP) are the main catecholamine of clinical interest, as they play crucial roles in the regulation of nervous and cardiovascular systems and are involved in some brain behaviors, such as stress, panic, anxiety and depression. Changes of catecholamine concentrations in organisms have a close connection with some neurological disorders and certain diseases. Therefore, there is an urgent need for a reliable sensing device able to provide their continuous monitoring in a minimally invasive manner [4].

In this work, we present the first highly nanoporous gold (h-nPG) microneedles-based sensor for minimally invasive monitoring of catecholamine in ISF.

The highly nanoporous microneedles-based gold electrode was prepared by a simple electrochemical self-templating method that involves two steps, gold electrodeposition and hydrogen bubbling at the electrode, which were realized by sweeping the potential between +0.8 V and 0 V vs Ag/AgCl for 25 scans in a 10 mM $HAuCl_4$ solution containing 2.5 M NH_4Cl, and successively applying a fixed potential of -3 V vs. Ag/AgCl for 60 s [5]. The resulting microneedles-based h-nPG sensor displays an interference-free catecholamine detection without compromising its sensitivity, stability and response time.

The performance of the h-nPG microneedles array sensor for total catecholamine detection was successively assessed in artificial interstitial fluid and in a hydrogel skin model, both spiked with NEP, at typical physiological concentrations.

Keywords: microneedles; wearable sensor; catecholamine; dopamine; epinephrine; norepinephrine; continuous monitoring.

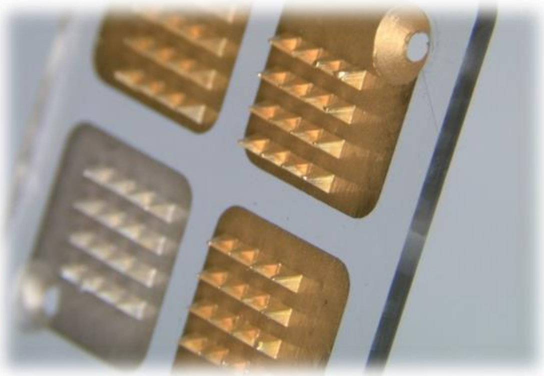


Figure 1: Microneedles array (2.5x2.5x0.2 cm) consisting of a polycarbonate structure with 4 microneedles arrays (16 pyramidal microneedles, base 0.06 cm, height 0.1 cm).

References:

1. A.E.G. Cass, S. Sharma, *Meth. Enzymol.*, **2017**, *589*, 413.
2. L. Ventrelli, L.M. Strambini, G. Barillaro, *adv. Healthcare Mater*., **2015,** *4*, 2606.
3. T.M. Rawson, S. Sharma, P. Georgiou, A. Holmes, A.E.G. Cass, D. O'Hare, *Electrochem. Comm.*, **2017**, *82*, 1.
4. J.A. Ribeiro, P.M.V. Fernandez, C.M. Pereira, F. Silva, *Talanta*, **2016,** 160, 653.
5. P. Bollella, S. Sharma, A.E.G. Cass, F. Tasca, R. Antiochia, *Catalysts*, ***2019***, *9*, 580.

Ionized Gas Defelction Gyroscope

Matthew C. Stewart[1*], Xuehan Liu[1] and Albert M. Leung[1]
[1] School of Engineering Science, Simon Fraser University, Burnaby, Canada

Abstract:

We present an experimentally verified new gyroscope based on deflection of ionized gas in a confined volume. This gyroscope makes improvements over previous designs in simplicity, robustness and power consumption. A number of jet flow gyroscopes have been developed using hotwire anemometers to measure fluid flow deflection[1-3]. The key differentiator of our gyroscope is the elimination of hotwire anemometers. In the ionized gas deflection gyroscope, the jet is deflected while ionized. By splitting a mesh cathode into two sections and measuring the current difference, we determine the deflection within the ion wind generator instead of as a separate step.

The illustration below shows a conceptual illustration of our design (Figure 1). The device is in a sealed 54 cm^3 chamber filled with air at atmospheric pressure. A high voltage of 3.8 kV is applied to the needle anode to produce a corona discharge with a total current of 1.0 µA. The created ions are moved by an electric field to the stainless steel mesh cathodes at earth potential 16.0 ± 0.5 mm away. Each cathode is rectangular with a height of 24 mm and a width of 14 mm. The mesh is composed of 120 µm diameter woven steel wire. The cathodes are separated by less than 1 mm.

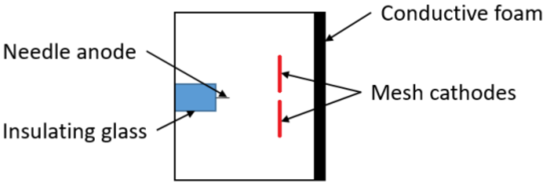


Figure 1: Conceptual diagram of ionized gas deflection gyroscope.

The ions move towards the cathodes while colliding with the neutral molecules and imparting them with momentum, creating a flow of moving air and ions. If the system is rotating, this flow is deflected by the Coriolis force. Since the ions are deflected along with the air, a measured difference between the currents into the two cathodes is observed. By measuring this difference in currents, we determine the magnitude of deflection which relates directly to angular velocity.

The results of spinning the above device are presented here (Figure 2). An overall gain of 0.28 nA/(°/s) is achieved. With a noise and interference floor of less than 0.028 nA/(°/s), we have a sensing resolution of 36°/s.

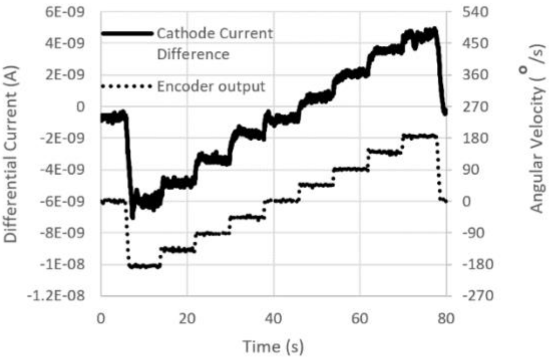


Figure 2: Experimental results demonstrating successful measurement of rotation.

This device already shows promising results in power consumption at 4 mW and sensitivity at 36°/s. We believe these parameters can and will be significantly improved through optimization, noise reduction and further experimentation. The chamber dimensions have not been optimized and we expect that they can be significantly reduced. Our device’s small size, low power, robustness, simplicity and lack of a need of any exotic materials all lead to high potential for eventual commercialization.

Keywords: gyroscope, inertial sensors, ion wind, corona discharge.

References:

1. Takemura, K. et al. (2008) A liquid rate gyroscope using electro-conjugate fluid, *Sens. Actuators A: Phys.*, vol. 149, no. 2, pp. 173-179.
2. Dau, V. T., Dao, D. V., Shiozawa, T., Sugiyama S. (2007) Convective gas gyroscope based on thermo-resistive effect in Si pn junction, *Transducers and Eurosensors, Lyon, France*, pp. 2525-2528.
3. Dau, V. T., Dinh, T. X., Tran, C. D., Bui, T. T., Phan, H. T. (2018) A study of angular rate sensing by corona discharge ion wind, *Sens. Actuators A: Phys.*, vol. 277, pp. 169–180.

Surface-Enhanced InfraRed spectroscopy for selective and sensitive detection of organophosphorus compounds

P. Fehlen[1,2], G. Thomas[1], F. Gonzalez-Posada Florès[2], T. Taliercio[2], D. Spitzer[1]
[1]NS3E-CNRS-UMR3208 French-German Research Institute of Saint-Louis, 5 rue du Général Cassagnou 68301 Saint Louis France
[2]IES-CNRS-UMR5214, 860 rue Saint Priest 34095 Montpellier France, Pierre.FEHLEN@isl.eu

Abstract:

Organophosphorus compounds (OPs) include chemical warfare agents (CWAs) which represents an increasingly real threat to soldiers and the civilian population. The ability to detect minute amounts of these molecules in air with a fast response, high sensitivity, and high selectivity becomes necessary. However, until now, current means of detection of CWAs are either bulky, expensive, or lack selectivity; the latter being of crucial importance in field conditions.

Infrared (IR) spectroscopy is a well-known selective detection technique, but taking into consideration the extremely low concentration levels (ppb) required for efficient detection of CWAs, the sensitivity threshold must be enhanced. To achieve this goal, we use an epsilon-near-zero-based perfect absorber plasmonic chip made of III-V semiconductors ($InAs_{0.91}Sb_{0.09}$); whose plasmonic response, associated with a locally highly-enhanced electrical field near the plasmonic nano-antennas (processed using either photolithography or electron-beam lithography), is tuned to the absorption lines of the CWA sarin mimic dimethyl methylphosphonate (DMMP).

Furthermore, CWAs such as the sarin gas are volatile. To overcome the challenge of gas-phase detection, we make use of surface chemistry to selectively and locally capture the molecules in the vicinity of the plasmonic nano-antennas, *in fine*, improving both the selectivity and the sensitivity of the detection. Surface chemistry consists of a self-assembled monolayer passively deposited in a liquid phase.

First results, aiming at detecting (i) the deposited monolayer and (ii) DMMP capture at the surface, indicate surface modification. Various surface functionalization are currently under study, then exposure tests in gas phase will be performed. This strategy promises significant improvements over existing sensors, especially toward higher sensitivity and integration.

Keywords: plasmonics, gas sensing, III–V semiconductors, infrared spectroscopy, surface-enhancement, epsilon-near-zero, surface chemistry, organophosphorus compounds, chemical warfare agents.

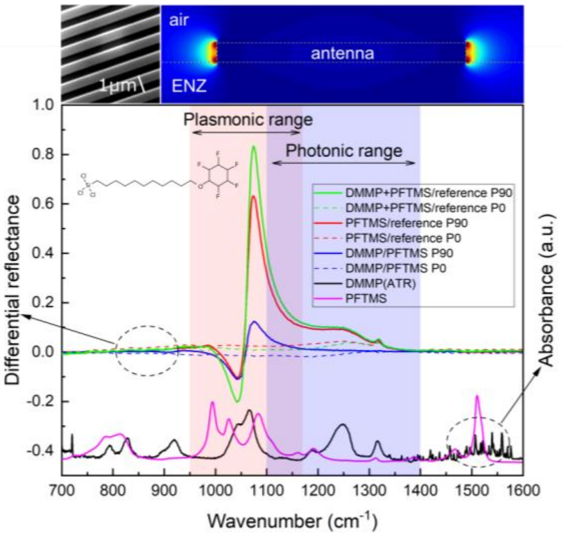


Figure 1: Top left: SEM image of the plasmonic nano-ribbons. Top right: x-axis normalized electric field. Differential spectra ($\vec{E}$ polarisation P90: perpendicular to ribbons, P0: parallel to ribbons) $I_2/I_1 - 1$ before and after functionalization (PFTMS: top left inset), and after exposure to DMMP. Red area: width of the plasmonic resonance: sensitive range. Blue area: Fabry-Perot cavity effect.

SIM Card-Type Responsive Polymer-Modified Paper-Based Biosensor for the Point-of-Care Determination of Creatinine in Urine

E. Tzianni[1], M. Trachioti[1], A. Lazanas[1], A. Florou[1], I. Moutsios[2], D. Moschovas[2], A. Avgeropoulos[2], K. Govaris[3], L. Panagiotidis[3], S. Panagiotidou[3], M. Prodromidis[1,]*

[1] Laboratory of Analytical Chemistry, University of Ioannina, 45 110 Ioannina, Greece
[2] Department of Materials Science Engineering, University of Ioannina, Greece
[3] Etris electronic applications, 61100 Kilkis, Greece

Abstract:

The development of medical diagnostic devices for point-of-care (POC) applications is of immense interest towards the establishment of decentralized health-care systems. The cost of miniaturized transducers, the need for elaborated modification of the sensing surface and the complexity of the assay workflow impede the widespread use of current biosensing technologies to POC applications.

Herein, we report on the synthesis and characterization of pH responsive copolymers of methacrylic acid (MAA) and methylmethacrylate (MMA) at different MAA/MMA ratios and molecular weights, and their use in the development of a sim card-type responsive copolymer-modified paper-based biosensor for the point-of-care, drop volume determination of creatinine in urine. A vertical microfluidic channel was fabricated on a paper strip by wax printing. The channel was blocked by depositing 2 μL of PMAA/PMMA copolymer (0.25-3% w/v in isopropanol/water 97/3 v/v). Atop of the dry copolymer/paper surface, creatinine deiminase was immobilized by physical adsorption. The functionalized paper strip was sandwiched between two conductive tapes from which the top one was hole patterned to serve as a dosing well (50-150 μL) for the microfluidic channel. Data demonstrated, on the one hand, infinity resistance to vertical flow of the urine sample though the enzyme-free biosensor, and on the other hand, in the presence of immobilized creatinine deiminase, a creatinine concentration dependent flow rate due to the degradation of the pH responsive PMAA/PMMA copolymer by the enzymatically produced ammonia, as a result of the action of creatinine deiminase on creatinine. Under selected experimental variables, the detection range of the device was tuned [1] over 3-30 mM creatinine that covers the normal range of creatinine (5-17 mM) in urine. The biosensor was assembled on a SIM card holder incorporating a third conductive strip, which in combination with a low-cost reading unit (BioPoC device, Figure 1) offers an automatic on/off (addition of the sample/degradation of the membrane) function for the measuring of the degradation time, and a screen for displaying the determined concentration. The device was applied to the drop-volume determination of creatinine in 1+1 diluted urine sample (adjusted to pH 6.5). The relative error (%) with respect to a hospital method was <8.1%.

Keywords: Point-of-care medical diagnostic device; Responsive polymers; Creatinine determination; Hunam urine samples;

Figure 1: The BioPoC prototype.

Acknowledgment: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-03341).

Reference:

1. Tzianni, E., Hrbac, J., Christodoulou, D., Prodromidis, M. (2020), A portable medical diagnostic device utilizing free-standing responsive polymer film-based biosensors and low-cost transducer for point-of-care application, *Sens. Actuators B*, 304, 127356

Ultra-Wideband Microstrip Patch Sensor Antenna Embedded into Bra for Comfortable Breast Cancer Microwave Imaging

Abel Rangel-Trejo[#1], José A. Bernardo[#1], L. Konadu [#1], Latifa Fakri-Bouchet[#1, #2]

[#1] Univ Lyon, CNRS, Université Claude Bernard Lyon 1,
Institut des Sciences Analytiques, UMR 5280, 5 rue de la Doua,
F-69100 VILLEURBANNE, France
[#2] INSA Lyon, France

Abstract:

An Ultra-Wideband (UWB) Microstrip Patch Sensor Antenna of size 12 mm x 18 mm is proposed in this study. This is a promising sensor for incorporation into a bra fixture for comfortable breast cancer Microwave Imaging (MWI), essential for users with advanced cancer stage [1].

The compact size, effective-cost, and easy-fabrication of this antenna, makes it a good candidate for high-density antenna array sensor system for enhancement of microwave image resolution. Additionally, this antenna is designed to work in the complete frequency range of the overlapping unlicensed spectrum frequencies defined by the FCC (in USA) and ETSI (in Europe) from 3.4 to 8.5 GHz [2]. The sensitivity as well as all other performance parameters are initially compared to those of a typical Microstrip Patch Antenna [3]. The antenna evaluation is done by parametric design analysis, making comparison of different dielectric substrates, dimensions, and manufacturing reproducibility techniques. The repeatability includes 15 fabricated antennas with the same compact size, fabricated in FR-4 substrate of 1.6 mm thickness with 35 µm of conductive-copper layer thickness (Figure 1). The sensor experimental results showed an UWB of ~ 11 GHz resonance Bandwidth starting from 2.9 GHz up to 14.09 GHz, corresponding to a functional fractional bandwidth of more than 130%. The antenna achieved a minimum Reflection coefficient $S_{1,1}$ of -29.15 dB, maximum Transmission coefficient $S_{2,1}$ of -31.77 dB, Gain of -0.63dBi and radiation efficiency of 42% at 3.464 GHz (Figure 2). This study will provide the basis for continue the gain increase & sensor evaluation of its imaging capabilities using heterogeneous Breast Phantoms for MWI pre-clinical medical trials, perfect to continue with large-sale trials, industrial involvement, and market launch as a medical device for the whole society.

Keywords: Breast-Cancer, Oncology, Microstrip Patch antennas, Microwave imaging, Microwave measurement, Radar Imaging, Ultra-Wide-Band.

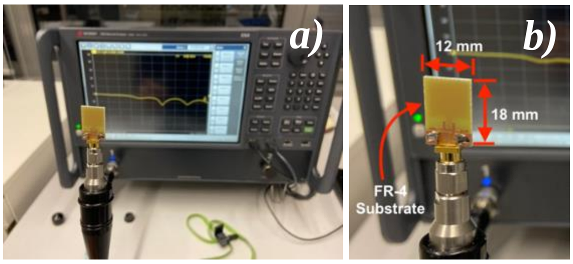


Figure 1: Fabricated Ultra-Wideband Microstrip Patch Sensor Antenna ***a)*** in connectivity to SMA connector for VNA S-parameter measurements, and ***b)*** zoom with dimensions and substrate specification.

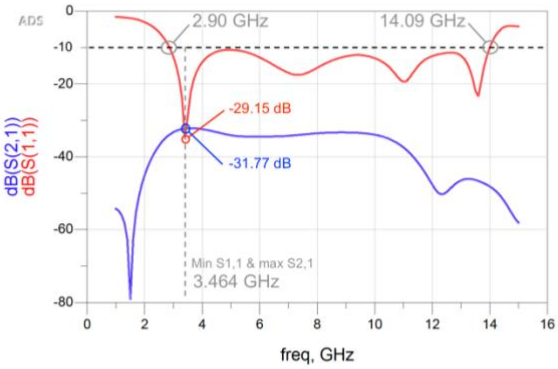


Figure 2: $S_{1,1}$ and $S_{2,1}$-parameteres of UWB Microstrip Patch Antennas at 10 cm distance (front-facing) in free-space measurement.

References:

1. R. Benny, T. A. Anjit, and P. Mythili, “An Overview of Microwave Imaging for Breast Tumor Detection,” *PIER B*, vol. 87, pp. 61–91, 2020.
2. A.-D. Capobianco *et al.*, “Directive Ultra-Wideband Planar Antennas,” in *Microwave and Millimeter Wave Technologies Modern UWB antennas and equipment*, I. Minin, Ed. InTech, 2010.
3. C. A. Balanis, *Antenna theory: analysis and design*, 3. ed. Hoboken, NJ: Wiley-Interscience, 2005.

New Methodology to Improve an Implantable Micro-sensor for NMR Spectroscopy

José A. Bernardo[1], Abel Rangel-Trejo[1], Adam Adewolu[1,4], Lucas Werling[2], Wilfried Uhring [2], Luc Hebrard[2], Christian Gontrand[3,4], Latifa Fakri-Bouchet[1,4]

[1]Univ Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences Analytiques, UMR 5280, 69100 Villeurbanne, France, [2]Université de Strasbourg, ICube Laboratory, 67037 Strasbourg, France, [3]INL (Institut de Nanotechnologies de Lyon), 69621, Villeurbanne, [4]INSA Lyon, France

Abstract:

The opportunity to predict and optimize from the expected performances (high Q factor and Signal to Noise Ratio SNR) the geometry of the NMR microprobe would lead to the manufacture of different desired geometries (Rectangular, Ellipsoidal, Square and Circular) with the optimal dimensions. In our case, the needle micro-coil (micro-coil + Transmission Line + connecting path, **Fig. 1**) is dedicated to the detection of small samples and low concentrations of analytes, using localized NMR spectroscopy (MRS). One of the main challenges of MRS is to improve its sensitivity and spectral resolution in the case of weak metabolites concentration in a small region of interest (ROI ~ 2µL-3µL). One way to increase this sensitivity is to miniaturize the NMR receiver i.e to adapt the coil to the sample dimensions improving the SNR. We can also enhance the Needle micro-coil performance by improving the microfabrication technology after predicting an optimal micro-coil geometry [1].

In this perspective, we have proposed a 3D-TLE platform, which is a homemade software developed on MATLAB. We also proposed an Artificial Neuronal Network (ANN) to carry out the design [2, 3]. The 3D-TLE allows the extraction of each electrical parameter (RLC) from the complete electrical circuit to model the microprobe that we carried out previously on two types of substrates (glass and silicon).

Implementing the developed ANN process before the micro-manufacturing process leads to peak performance faster and more accurately. Our ANN model was trained validated and tested using data generated by the 3D-TLE platform (6528 data samples). For example, we can notice in **Fig. 2**, the prediction of the microprobe Q-factor which matches well with the true data.

Throughout our study, we demonstrated that our 3D-TLE platform combined with Machine Learning represent a new and powerful tool to improve NMR microprobes performances.

Keywords: ANN, ML, NMR Spectroscopy, SNR, Micro-coil, 3D-TLE.

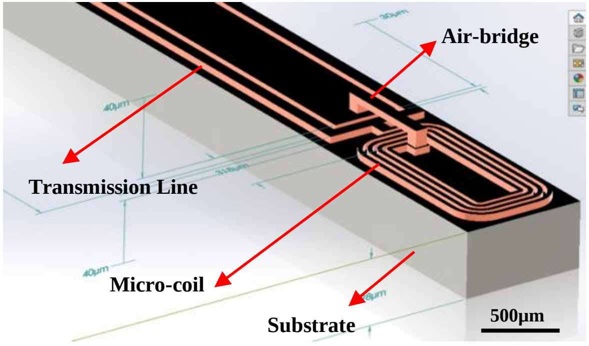


Figure 1: The 3D design of the microprobe

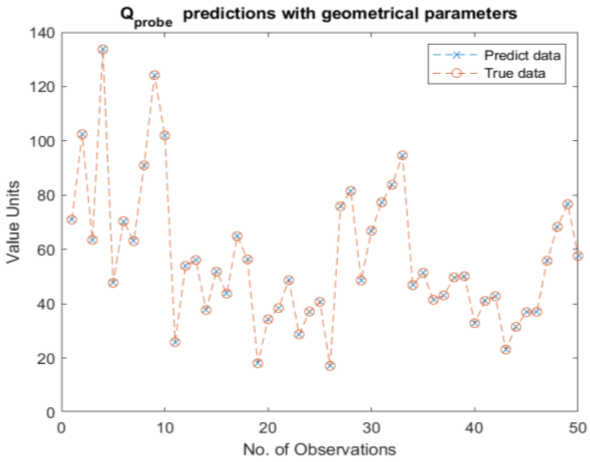


Figure 2: The microprobe Q factor prediction and the true value

References:

[1] N. Baxan *et al.*, “Limit of detection of cerebral metabolites by localized NMR spectroscopy using microcoils,” *Comptes Rendus Chimie*, vol. 11, no. 4–5, pp. 448–456, Apr. 2008.

[2] Y. Ma, “Modèles compacts électroniques du premier ordre et considération de bruit pour les circuits 3D,” PhD thesis, INSA of Lyon, France, 2018.

[3] A. Nabil *et al.*, “Electrical modeling of tapered TSV including MOS-Field effect and substrate parasitics: Analysis and application,” *Microelectronics Journal*, vol. 100, p. 104797, Jun. 2020.

Self-Assembling DNA Hairpins for Enzyme-Free Detection of Nucleic Acids in Point-of-Care Applications

J. W. Beard [1*], S. L. Hunt [2], B. L. Miller [1,2]
[1] Department of Biomedical Engineering, University of Rochester, Rochester, United States
[2] Department of Dermatology, University of Rochester, Rochester, United States

Abstract:
From cancer screenings to acute viral infections, sensitive and accurate detection of nucleic acid sequences plays an important role in diagnostics. The most widely used assays for nucleic acid detection (polymerase chain reaction and loop-mediated isothermal amplification) rely on environmentally sensitive enzymes that are difficult to maintain in point-of-care (POC) applications. We explore how custom designed metastable DNA hairpins can bring nucleic acid testing to the patient's bedside using a technique called hybridization chain reaction[1] (HCR). HCR, previously employed for viewing mRNA *in situ*[2], requires a minimum of two ssDNA sequences strategically engineered to form hairpin-like secondary structures with complimentary regions that will promote a cascade of hairpin-to-hairpin hybridization when in the presence of a target nucleic acid sequence. In our work, the H1 and H2 hairpins (Figure 1) are conjugated with a donor and acceptor fluorophore, respectively, for a FRET pair capabable of producing a fluorescent signal when hybridized in the copolymer assembly. This self-assembling DNA hairpin technique allows us to significantly amplify a fluorescent signal from a single nucleic acid sequence without the use of enzymes or thermocycling, making it ideal for POC diagnostics. We will discuss strategies for designing DNA hairpin probes and FRET schemes for optimizing HCR mediated detection of HIV RNA in POC settings.

Keywords: point-of-care, HIV, diagnostics, nucleic acid amplification, hybridization chain reaction, DNA origami, fluorescence microscopy, FRET, low-resource settings.

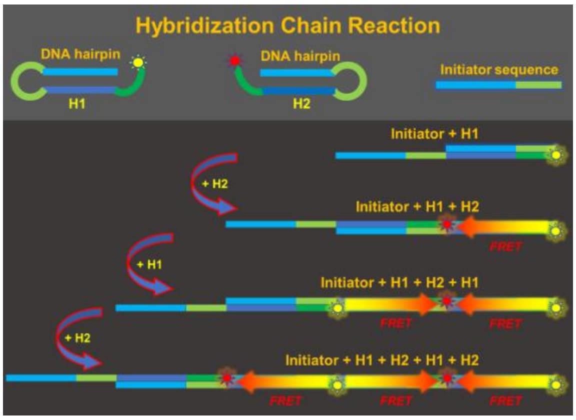


Figure 1: Schematic of hybridization chain reaction using Förster Resonance Energy Transfer (FRET) for fluorescence detection of a target initiator sequence. H1 has a complementary region to the initiator sequence, causing it to unfold from its secondary structure and hybridize with the initiator, exposing a complementary sequence to H2. H2 hybridizes with H1, exposing a complementary sequence to H1, thus continuing the cascade. The intensity of the H2 acceptor fluorophore is dependent on the length of the H1/H2 HCR product.

References:

1. Dirks RM, Pierce NA. Triggered amplification by hybridization chain reaction. *Proc Natl Acad Sci U S A*. 2004;101(43):15275-15278. doi:10.1073/pnas.0407024101
2. Shah S, Lubeck E, Schwarzkopf M, et al. Single-molecule RNA detection at depth by hybridization chain reaction and tissue hydrogel embedding and clearing. *Dev*. 2016;143(15):2862-2867. doi:10.1242/dev.138560

Smart Materials & Surfaces - SMS 2021 Onsite Session II

$(Sn,Ti,Nb)_xO_2$ Solid Solution: an Innovative Sensing Material for H_2 Detection

E. Spagnoli[1], A. Gaiardo[2], B. Fabbri[1], M. Valt[1], S. Krik[1], M. Ardit[1], G. Cruciani[1], M. Della Ciana[1,3], L. Vanzetti[2], S. Gherardi[1], P. Bellutti[2] , G. Vola[4] , C. Malagù[1], V. Guidi[1]
[1] Department of Physics and Earth Sciences, University of Ferrara, Ferrara, Italy
[2] MNF - Micro Nano Facility unit, Sensors and Devices center, Bruno Kessler Foundation, Trento,Italy
[3] National Research Council, Institute for Microelectronics and Microsystems, Bologna, Italy
[4] Cimprogetti S.r.l. Lime Technologies, Bergamo, Italy

Abstract:
The interest in chemoresistive gas sensors has grown over the years because robustness, sensitivity, cost-effectiveness and small size make them attractive for a wide range of applications. These devices are composed by a sensing film, usually nanostructured semiconducting metal oxides (SMOXs), deposited on an inert substrate and equipped with control circuitry. The sensing material changes its electrical resistance as a result of redox reactions occurring between the nanomaterial surface and the target gas. Recently, great attention has been paid to nanostructures solid solutions based on metal oxides to enhance the sensing performance with respect to those of single-oxide counterparts. As an example, tin and titanium oxides (SnO_2 and TiO_2) are wide-gap n-type semiconductors extensively investigated for the fabrication of chemoresistive devices for gas sensing applications. However, their sensing performance is often unsatisfactory, especially in terms of selectivity and limit of detection. Tin and titanium oxides would easily form solid solutions because they can exhibit a rutile type structure where octahedrally coordinated Ti^{4+} and Sn^{4+} have similar ionic radii (i.e. 0.605 Å and 0.69 Å, respectively). Such solid solution combines the positive qualities of singles oxides, e.g. high sensitivity towards reducing gases and low influence by humidity [1,2].

Addition of metals to a sensing material may also be beneficial. The effect of Nb addition on H_2 sensing properties of $(Sn,Ti)_xO_2$ will be presented. $(Sn,Ti,Nb)_xO_2$ powders were synthetized through co-precipitation by keeping the Sn/Ti proportion constant at the optimal value for sensing performance, while changing Nb content and calcination temperature. Powder composition, structure and morphology were investigated by different techniques. Observations at SEM microscopy revealed that the morphology consists of rounded nanoparticles (see Fig. 1, above) and X-ray powder diffraction analyses confirm that $(Sn,Ti,Nb)_xO_2$ samples were a solid solution with rutile-type structure. Electrical characterization of the films shows high sensitivity and marked selectivity towards H_2 (Fig. 1, below).

Keywords: Solid solution, SMOXs-based sensor, H_2 sensor.

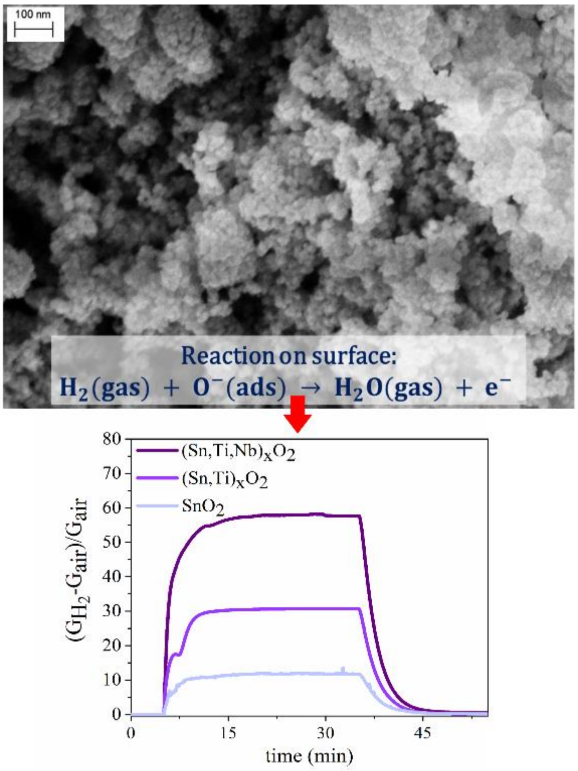


Figure 1: Figure illustrating the morphology of $(Sn,Ti,Nb)_xO_2$ powders (above) and the response of $(Sn,Ti,Nb)_xO_2$, $(Sn,Ti)_xO_2$ and SnO_2 sensors to 50 ppm of H_2 as a consequence of H_2 reaction on surface (below).

References:

1. C. Malagù, V. Guidi, M.C. Carotta, G. Martinelli, Appl. Phys. Lett. **84**, (2004) 4158
2. M.C. Carotta, et al., *Sensors and Actuators B* **139** (2009) 329–339

Bioorthogonal SERS nanotags for multiplex detection of biomolecules: a versatile straightforward method towards multicolor-custom palette

C. Dallari[1], R. Innocenti[1], E. Lenci[2], A. Trabocchi[2], F.S. Pavone[1,3,4], C. Credi [1,4*]

[1] European Laboratory for Non-Linear Spectroscopy, University of Florence, Sesto Fiorentino, Italy
[2] Department of Chemistry, University of Florence, Sesto Fiorentino, Italy
[3] Department of Physics, University of Florence, Sesto Fiorentino, Italy
[4] National Institute of Optics, National Research Council, Sesto Fiorentino, Italy

Abstract:

Surface enhanced Raman spectroscopy (SERS) constitutes the most promising analytical method as alternative to traditional detection bioassays. In this sense, SERS has been extensively exploited for the development of diagnostic optical assays capable of identifying early-stage pathological conditions through the molecular screening of biological fluids and tissues. Moreover, owing to its high sensitivity and multiplexing capability, SERS has gained rising attention for biosensing assays especially for those diseases whose early-stage diagnosis relies on the ratio of more than one biomarker. However, biosensing applications of SERS multi-labelling could be restricted by standard Raman reporters (RRs) whose spectra profiles are characterized by multiple shifts in the fingerprint region possibly overlapping with background signals from endogenous biomolecules. To overcome these limitations, recent studies reported about a novel class of Raman tags characterized by bioorthogonal spectral signatures with narrow peaks in the biologically Raman silent region (1800 cm^{-1} ÷ 2600 cm^{-1}). In the present work, a versatile and straightforward method is presented to synthesize a novel palette of bioorthogonal RRs whose chemical structure is properly engineered to work as optimal SERS nanotags. Starting from common cysteine amino acid, the RRs are synthesized to have thiol end-chain groups for covalently binding to gold nanoparticles (NPs) as well as to have aromatic rings in the backbone structure and to co-work as NPs-capping agents with PEG molecules. RRs NPs-loading was optimized to guarantee the highest signal deriving from Alkyne- and Cyano-derived RRs end-chain groups acting as strong NIR emitting Raman signals while SERS nanotags morphology and colloidal stability was verified over time. Systems sensitivity was quantified by implementing multiplexing analysis against synthetic biological fluids as well as with cell cultures. To this end, selective biological tags can be achieved by further assembling antibodies on RRs-NPs surfaces decorated with carboxyl groups deriving from PEG molecules. Biological multiplex validation demonstrates the potentiality of SERS nanotags for multiple biomarkers detection while the versatility of RRs synthesis provide a straightforward method to easily prepare multi-color custom SERS nanoprobes.

Keywords: Surface enhanced Raman spectroscopy, gold nanoparticles, SERS nanotags, bioorthogonal Raman reporters, multiplexing analysis, optical biosensors.

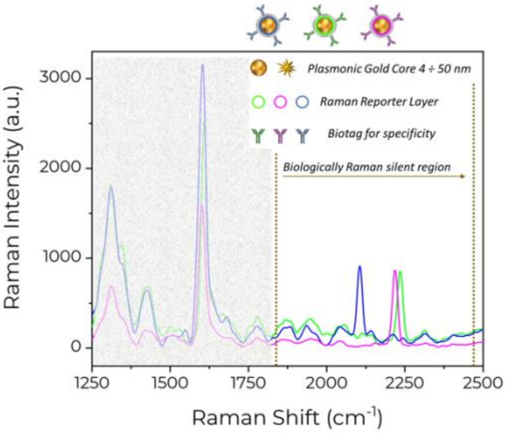


Figure 1: Representative Raman spectra of bioorthogonal RRs characterized by narrow peaks in the biologically Raman silent region.

References:

1. Pal, S., Ray, A., et al. (2019) DNA-enabled rational design of fluorescence-Raman bimodal nanoprobes for cancer imaging and therapy. *Nat Commun 10, 1926.*
2. Montoneri, F., et al. (2012) Multiplex targeted in vivo cancer detection using sensitive near-infrared SERS nanotags, *Nano Today*, 7, 85—93.
3. Wang, J., Liang D. et al. (2020) Bioorthogonal SERS Nanotags as a Precision Theranostic Platform for in Vivo

SERS Imaging and Cancer Photothermal Therapy, *Bioconjugate Chem*., 31, 182−193.

Anisotropic iridescence and polarization patterns in a direct ink written chiral photonic polymer

Jeroen Sol[1,*], Henk Sentjens[1], Lanti Yang[2], Nadia Grossiord[2], Albert Schenning[1], Michael Debije[1]
1) Stimuli-responsive Functional Materials and Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands
2) T&I, SABIC, Bergen op Zoom, The Netherlands

Abstract:
The iridescence and polarization characteristics of structural color originate from the nanoscale organization of materials. A major challenge in materials science is generating the bright, lustrous hues seen in nature for use in functional polymer materials. In previous work, the molecular director profile in a chiral nematic liquid crystal could be distorted through a combination of tuning the liquid crystal and processing.[1] Here, we show the synthesis of a chiral nematic liquid crystal oligomer ink for bar coating and direct ink writing (DIW), a 3D printing technique, with novel optical behavior after material deposition.[2]

After deposition the ink self-assembles into a visible light-reflective, chiral photonic structure. Shear flow during deposition leads to a distorted helicoidal structure of the liquid crystals. As a result, the photonic material's longest reflected wavelength is offset from the material's normal direction at an angle of about 50° (see Figure 1ab). Following from the slanted cholesteric helix is that at normal incidence, the characteristic circular polarization selectivity is strongly diminished.[3] Bar coating allows for generation of this optical behavior over large, multiple cm² surfaces; with DIW, we are able to program the optical characteristics on a voxel-by-voxel basis (Figure 1c) to freely write our material into a variety of shapes (Figure 1d). The ink can be crosslinked using ultraviolet light to form an elastic polymer coating or free-standing object in which the programmed optical characteristics are fixed into the molecular network. We will show that with UV-crosslinking through a photomask, additional freedom in design is gained.

This material's spatially tunable optical properties, both in the presence of selective reflection and the photonic axis of it, make it suitable for use in anti-counterfeiting security tags, as optical elements in 3D printed soft robots, decorative elements, or as incidence angle-dependent reflective coatings.

Keywords: cholesteric liquid crystal, direct ink writing, photonic material, chiroptical material, tunable optics, polarization selectivity

References:

1. Kragt, A. J. J., Hoekstra, D. C., Stallinga, S., Broer, D. J. & Schenning, A. P. H. J. 3D Helix Engineering in Chiral Photonic Materials. *Adv. Mater.* **31**, 1903120 (2019).
2. Sol, J. A. H. P. *et al.* Anisotropic iridescence and polarization patterns in a direct ink written chiral photonic polymer. *Adv. Mater.* 2103309 (2021) doi:10.1002/adma.202103309.
3. Lee, K. M. *et al.* A Different Perspective on Cholesteric Liquid Crystals Reveals Unique Color and Polarization Changes. *ACS Appl. Mater. Interfaces* **12**, 37400–37408 (2020).

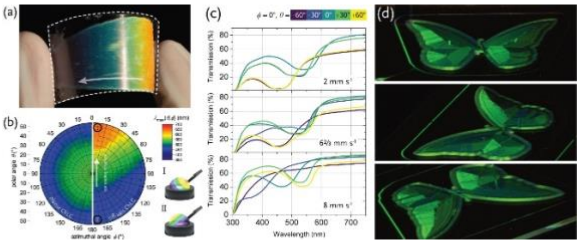


Figure 1. a) Crosslinked photonic film bar coated and polymerized on a flexible plastic substrate displaying axially asymmetric color reflection. b) Two-dimensional optical characterization of reflected light for a conventional chiral nematic reflector (left) and the slanted chiral nematic presented here (right). "I" and "II" illustrate the detector arm orientation with respect to the perspective-dependent reflected wavelength. c) Angle-dependent UV-vis transmission spectra for material strips printed at 2, 6²/₃, and 8 mm s^{-1} ($-60° > \theta > +60°$, azimuthal angle $\phi = 0°$). d) Butterfly structure printed at 10 mm s^{-1} observed from different viewing perspectives, highlighting the compartmentalized optical responses.

Photocatalytic activity of TiO_2 immobilized on Corona pre-treated polypropylene films

R.Rescigno [1], O.Sacco [1], R.Fittipaldi[2], V.Venditto[1], V.Vaiano[3], C.Daniel[1]

[1] Department of Chemistry and Biology “A. Zambelli”, University of Salerno, Fisciano, Italia
[2]CNR-Spin, c/o University of Salerno, Fisciano, Italia
[3] Department of Industrial Engineering, University of Salerno, Fisciano, Italia

Abstract:

In last years the immobilization of TiO_2 on different types of supports substrates has been drawing a lot of attention because it eliminates the need of costly post-treatment separation processes[1]. However the methods for anchoring TiO_2 on the support strongly influence the titania photocatalytic activity depending on the type of substrate, and the pollutant to be removed. Therefore the methods keep the photocatalytic performances of TiO_2 intact are preferred. Among the substrates used to support TiO_2-based photocatalysts polymeric ones appear to be very promising. Different TiO_2/polymer composites based on conventional polymers have been prepared with different technique and characterized so far[2]. Some of these TiO_2/polymer composites showed a remarkably enhancement of the antibacterial properties[3]. The aim of this work is to achieve polypropylene films (PP) functionalized with a commercial TiO_2 (Degussa P25). In details, PP films treated with corona plasma were coated with TiO_2 by soaking the films in a suspension containing the photocatalyst in powder form. The corona pre-treatment is a practical and effective method to activate the surface by the introduction of negatively charged functional groups (COO-, –O–O-), which results in a better adhesion of photocatalyst[4]. The obtained coated films were characterized with different technique, e.g. SEM analysis (Figure 1), and the photocatalytic activity under UV light irradiation was analysed in the degradation of model organic pollutant (methylene blue, MB) in aqueous solution. The photocatalytic tests were carried out in a batch photoreactor irradiated by a UV lamp (nominal power of 8 W and wavelength emission 365 nm). The experimental results showed that the TiO_2 coated PP films allowed to achieve a MB discoloration of almost 25% after almost 2 h of UV irradiation. In contrast a unfunctionalized PP films did not shown any photocatalytic activity under the same irradiation conditions.

Keywords: titania (TiO_2), polypropylene (PP), corona plasma, coated films, methylene blu (MB), photocatalysis

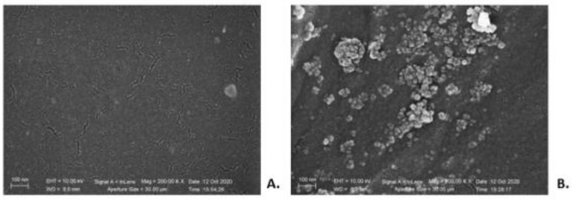


Figure 1: SEM images of surface morphologies of PP films before treatment (A.) and after treatment with TiO_2 suspension (B.)

References:

1. Vaiano, V., Sacco, O., Sannino, D. & Ciambelli, P. 2015. Nanostructured N-Doped TiO 2 Coated On Glass Spheres For The Photocatalytic Removal Of Organic Dyes Under UV or Visible Light Irradiation. Applied Catalysis B: Environmental, 170-171, 153-161.
2. Patra N, Salerno M, Cozzoli PD, Athanassiou A (2013) Surfactant-induced thermomechanical and morphological changes in TiO2-polystyrene nanocomposites. J Colloid Interface Science 1: 103-8.
3. Hashemabad Z N, Shabanpour B, Azizi H, Ojagh S M & Alishahi A (2017) Effect of Tio2 Nanoparticles on the Antibacterial and Physical Properties of Low-Density Polyethylene Film, Polymer-Plastics Technology and Engineering, 56:14, 1516-1527
4. Qi K , Xin J H , Daoud W A, Mak C L (2007) Functionalizing Polyester Fiber with a Self-Cleaning Property Using Anatase TiO2 and Low-Temperature Plasma Treatment, International Journal of Applied Ceramic Technology, 4 [6] 554–563

Co-Mn mixed oxides prepared by magnetron sputtering on stainless steel meshes as catalysts for the oxidation of volatile organic compounds

P.Topka [1,*], K. Jirátová [1], R. Perekrestov [2], M. Dvořáková [3], J. Balabánová [1], M. Koštejn [1],
D. Pokorná [1], M. Čada [2], Z. Hubička [2], F. Kovanda [3]

[1] Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Prague, Czech Republic
[2] Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic
[3] University of Chemistry and Technology, Prague, Czech Republic

Abstract:
Catalysts in the form of meshes possess a lot of advantages, especially low pressure drop and good heat transfer. Deposition of thin film of active phase on stainless steel meshes enables its high utilization in catalytic reaction due to low influence of internal diffusion of reactants and products. Oxides of Co and Mn show high catalytic activityh in various oxidation reactions. We have shown recently that the combination of magnetron sputtering and electrochemical deposition is a powerful tool to prepare highly active and stable catalyst for the oxidation of volatile organic compounds [1]. In the present study, we prepared Co-Mn mixed oxides supported on stainless steel meshes by magnetron sputtering of Mn or Co+Mn in the oxidation atmosphere, followed by calcination at 500 °C in air. The meshes were first pretreated by RF magnetron sputtering of Co to activate the metal surface. After that, a layer of Co_3O_4 (0.3 µm thick) was deposited electrochemically. The second layer was deposited by sputtering of Mn or Co+Mn in $Ar+O_2$ to prepare either MnO_x or mixed $CoMnO_x$ layers. Time of magnetron sputtering duration was changed to obtain different thicknesses of the MnO_x or $CoMnO_x$ layers (0.1, 0.2 or 0.3 µm). In addition, pure MnO_x and Co_3O_4 layers (thickness 2 µm) were prepared on meshes for comparison. In the total oxidation of ethanol, the activities of all sputtered catalysts were higher than that of the commercial pelletized Co-Mn-Al catalyst, although the content of the active components in the catalytic bed was more than 50 times lower. The highest catalytic activity exhibited the catalyst prepared by sputtering of MnO_x layer over electrochemically deposited Co_3O_4. The pure MnO_x catalyst supported on meshes showed the lowest temperature of 50 % ethanol conversion. However, two times higher amount of CO was formed over this catalyst in comparison with corresponding $CoMnO_x$ catalysts. Over the catalysts supported on meshes, the temperature required for 95 % conversion of ethanol to CO_2 was by ~100 °C lower in comparison with commercial Co-Mn-Al pellets.

Keywords: cobalt–manganese mixed oxides; magnetron sputtering; stainless steel meshes; ethanol oxidation; volatile organic compounds.

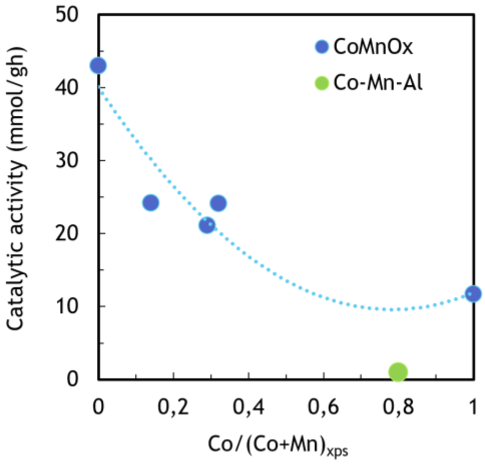


Figure 1: Dependence of relative catalytic activity on the Co:Mn ratio determined by XPS for the Co-Mn mixed oxides supported on stainless steel meshes (blue) compared to commercial Co-Mn-Al pelleted catalyst (green).

Acknowledgement: This research was funded by the TA CR, project number TN01000048.

References:

1. Dvořáková, M., Perekrestov, R., Kšírová, P., Balabánová, J., Jirátová, K., Maixner, J., Topka, P., Rathouský, J., Koštejn, M., Čada, M., Hubička, Z., Kovanda, F. (2019), Preparation of cobalt oxide catalysts on stainless steel wire mesh by combination of magnetron sputtering and electrochemical deposition, *Catal. Today*, 334, 13-23.

Development of thermo-responsive polymer coatings based on thiol-isocyanate chemistry to monitor the critical overheating of electronic devices

D. Bautista-Anguís [1], A. Wolfberger [1], S. Schlögl [1]

[1] PCCL Polymer Compentence Center Leoben, Roseggerstraße 12, 8700 Leoben, Austria

Abstract:

Nowadays, the complexity of electronic systems is constantly increasing due to demanding requirements of the market. Therefore, it is of crucial importance to guarantee their correct operation under challenging operating conditions. Special attention has to be focused on an early detection of possible overheating that could lead into an irreparable damage of the system, and in worst case lead to injuries.

The use of low-cost metal oxide (MOx) gas sensors, together with polymer coatings with thermally-labile functional groups, emerges as a novel and economically viable solution to monitor the critical over-temperatures.

A suitable approach is based on the synthesis of functional coatings by click-reaction between thiols and isocyanates to form thiourethanes, which at elevated temperatures (deblocking temperature) produces the initial reactants [1]. Selection of thiols with boiling points lower than the deblocking temperature allows the release of tracer gases that are easily detected with MOx sensors.

In the present work, different short-chain thiols were reacted with methylene diphenyl diisocyanate (MDI) to study the effect of the thiol structure on the deblocking temperature. This temperature was measured using well-known thermal techniques including differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and thermal desorption coupled to gas chromatography mass spectrometry (GC-MS), obtaining promising results in the range of 140°C-160°C (Figure 1).

The most promising thiol was furthermore implemented into a polyurethane-based coating by partially reacting polymeric MDI with the thiol followed by a full cross-linking with a suitable polyol. In order to obtain comparable results, the deblocking temperature and release of the thiol from the polyurethane matrix was measured with the above-mentioned techniques.

Keywords: thiourethane, thermo-responsive polymer, polymer coating, polyurethane, deblocking temperature, overheating, MOx gas sensors, click-chemistry, thiol, diisocyante, DSC, TGA, GC-MS.

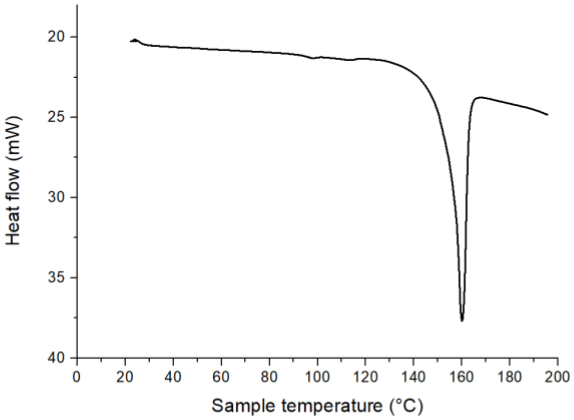


Figure 1: DSC test result of MDI blocked with 1-propanethiol. An endothermal peak in the range of 125-165 °C is observed as consequence of the deblocking reaction.

Reference:

1. Rolph, Marianne S., Markowska, Anna L. J., Warriner, Colin N. and O'Reilly, Rachel K. (2016); Blocked isocyanates: from analytical and experimental considerations to non-polyurethane applications; *Polym. Chem.,* 2016, 7, 7351.

Modelling and Finite Element (FE) simulation of photomechanical organic thin films

R. Cedeno [1], I. Arroyo[2], K. Kandil[1], S. Aloïse[2], M. Nait-Abdelaziz[1]

[1] UML, University of Lille, Lille, France
[2] LASIR, University of Lille, Lille, France

Abstract:
Recently, we elaborated novel photoactive thin films by combining functionalized diarylethene (DTE) and functionalized poly-ethylene butylene (PEB). The photomechanical effect is achieved thanks to the photoswitching property in the DTE molecule (Figure 1), while the elastomeric matrix (PEB) gives the thin film rubber-like behavior in addition to reversible deformation. An experimental setup for motion tracking was designed, combining a microscopic camera and visible (VIS) and UV light LEDs to activate the molecular switch. Several cycles of successive UV-VIS irradiation were recorded, showing bending deformation of the thin film. Through video processing analysis, we confirmed that photomechanical deformation was induced by light exposure in our thin films.

Our objective is to link the DTE photoswitching kinetics to the light-induced deformation of the thin film by using the photochromic kinetics model proposed by Pariani (1) for DTE-based crystals and the constitutive model Arruda-Boyce for rubber-like materials (2). These two models are implemented in the FE software Marc Mentat with user-external subroutines developed by us. The dependence of the photomechanical activation on parameters such as the light intensity and the optical and mechanical properties of the material was revealed by the FE simulations we performed. The mechanical model we implemented is based on the assumption of elastic deformation. Moreover, it will be necessary to consider the viscoelasticity of the elastomer, thus proposing a complete constitutive model that unifies the light-induced response at the molecular scale with the macroscopic deformation.

Keywords: photo-induced deformation, photoactive thin films, FE simulation, diarylethene

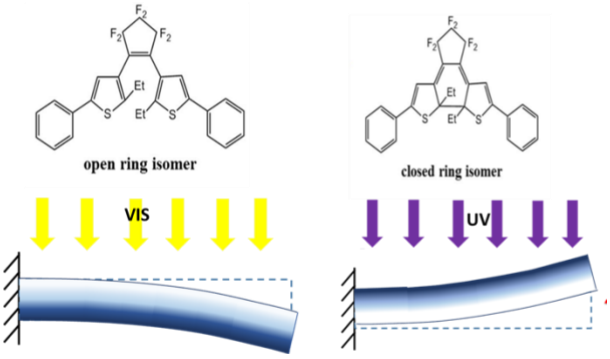


Figure 1: figure illustrating the switch effect of DTE molecules, giving two configurations: open form and closed form. This molecular change produces the photoinduced deformation of the thin films.

References:

1. G. Pariani, A. Bianco, R. Castagna, et C. Bertarelli, *Kinetics of Photochromic Conversion at the Solid State: Quantum Yield of Dithienylethene-Based Films*, J. Phys. Chem. A, vol. 115, nº 44, p. 12184-12193, Nov. 2011.
2. E. M. Arruda et M. C. Boyce, *A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials*, Journal of the Mechanics and Physics of Solids, vol. 41, nº 2, p. 389-412. Fev. 1993.

A novel crystallographic orientation-based methodology to elucidate the mechanical properties of zinc alloy coatings

Masoud Ahmadi [1,*], Bart J. Kooi [2],Yutao Pei [1]

[1] Department of Advanced Production Engineering, Engineering and Technology Institute Groningen, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands
[2] Nanostructured Materials and Interfaces, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

Abstract:
Characterization and testing of thin films and coatings are usually more challenging compared to that of the bulk materials. Most of the coatings utilized in automotive and household industries exhibit a few microns thickness which gives rise to the size effect and difficulty in determining the exact functional properties. Realizing a predictive and quantitative methodology to assess the mechanical properties and cracking tendency of zinc alloy coatings is of great importance to attain durable surface functionality. The properties of metallic based coatings have been addressed mostly qualitatively in the literature. This study uncovers the local micromechanical properties using a new quantitative methodology as briefly depicted in Figure 1. To this end, orientation imaging microscopy (OIM) and meticulous nanoindentation experiments are employed. In this study, we reveal the crystallographic orientation dependent properties of zinc alloy coatings. The potential of advanced characterization techniques to scrutinize the microstructure and mechanical performance of the metallic coatings has been elucidated.

Keywords: Methodology, thin coatings, mechanical properties, crystallographic orientation, characterization

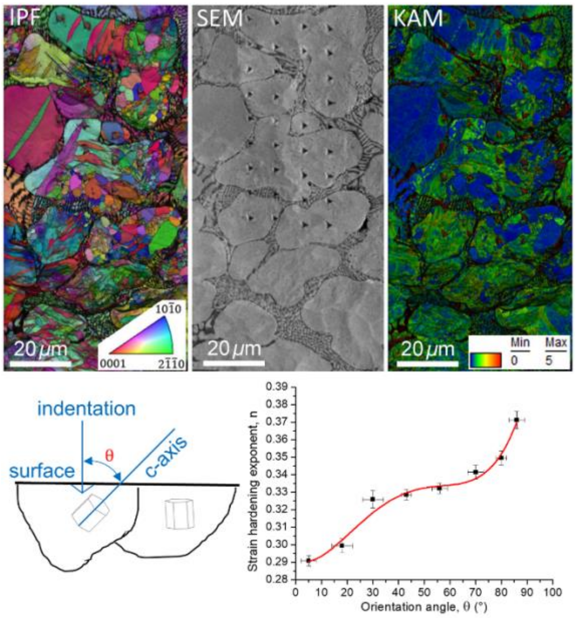


Figure 1: Novel correlation between crystallographic orientation and local micromechanical properties of zinc alloy coatings.

Integration of conductive fibers over wearable electronic textiles: Application of hydrogen evolution assisted (HEA) electroplating

Sabrina M. Rosa-Ortiz[1], Fatemeh Mokhtari[2], Arash Takshi[1] & Javad Foroughi[2,3]

[1]Department of Electrical Engineering, University of South Florida, Tampa, FL 33620, U.S.A.
[2]Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2500, Australia
[3]School of Electrical, Computer and Telecommunications Engineering Faculty of Engineering and Information Sciences, University of Wollongong, Wollongong, NSW 2522, Australia

Abstract:
While the electronic circuit manufacturing is well developed for fabricating circuits on solid and flat PCBs, the application of electroplating for the production of flexible and wearable electronics has been largely ignored, mainly due to the compact and rigid structure of deposited copper and the low deposition rate through the conventional galvanostatic (i.e. using constant DC current) method but with the advantages in the development of wearable and flexible electronics, there is an increasing demand for lightweight, flexible, energy storage, and wearable human and environmental monitoring systems with countless applications. To improve the conductivity of the structure, in this work, we study the feasibility of adopting the hydrogen evolution assisted electroplating method for patterning an electronic circuit on fabrics using a template of a conductive pattern applied via screen printing. The proposed method employs unique features in the metallization of the fabric with the HEA method. More importantly, the nanostructure on the deposited copper can diffuse to the fabric to produce a stable and well-adhered circuit layout to the substrate at room temperature. Recently, we have demonstrated the feasibility of making wearable piezo sensors by braiding polyvinylidene difluoride (PVDF) yarns in to a triaxial structure, which were produced by using a melt-spinning set-up and then placed at the Trenz-Export braiding machine for the development of triaxial braided piezoelectric PVDF fibers through a multi-step braiding.

Compared to the conventional electroplating, the HEA electroplating has an incredible speed of growing metals of 508 µm/s, generating structures of copper on the deposited area that can entangle the conductive pattern to the fabric for improvement of the adhesion of components and the integration of circuits to the triaxial fiber.

Keywords: Electrodeposition, copper electroplating, hydrogen evolution assisted electroplating (HEA), triaxial braided peizoelectric fibers, polymer, fabrics, printed circuit boards (PCBs).

A 0.4 mL of a conductive ink including multiwalled carbon nanotubes (MWNTs) was applied over the piezoelectric harvester (triaxial braided PVDF) to improve the copper deposition, which was possible to fulfill in less than 30 seconds. In previous work the triaxial braided PVDF yarn has shown extreme durability with no changes in its performance. Further studies showed some reduction in the flexibility of the structure after the copper deposition. However, the electrical resistance was significantly reduced. The results of this study show the feasibility of employing the HEA electroplating method for the development of highly conductive braided structures toward wearable electronics applications.

References:

1. Mokhtari, F., Foroughi, J., Zheng, T., Cheng, Z., & Spinks, G. M. (2019). Triaxial braided piezo fiber energy harvesters for self-powered wearable technologies. *Journal of Materials Chemistry A*, *7*(14), 8245–8257. https://doi.org/10.1039/c8ta10964h

2. Rosa-Ortiz, S. M., Khorramshahi, F., & Takshi, A. (2019). Study the impact of CuSO4 and H2SO4 concentrations on lateral growth of hydrogen evolution assisted copper electroplating. *Journal of Applied Electrochemistry*,*49*(12),1203–1210. https://doi.org/10.1007/s10800-019-01359-2

Generation of cytocompatible superhydrophobic Zr-Cu-Ag metallic glass coatings with antifouling properties for medical textiles

Elham Sharifikolouei[a*], Ziba Najmi[b], Andrea Cochis[b], Alessandro Calogero Scalia[b],
Maryam Aliabadi[c], Sergio Perero[a], Lia Rimondini[b]

[a] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca Degli Abruzzi 24, 10129, Turin (TO), Italy
[b] Department of Health Sciences, Center for Translational Research on Autoimmune and Allergic Diseases − CAAD, Università del Piemonte Orientale UPO, Corso Trieste 15/A, 28100 Novara (NO), Italy
[c] Competence Center Textile Chemistry,Environment, Energy, German Institutes of Textile and Fiber Research, 73770, Denkendorf,Germany

Abstract

Zirconium-Copper-based metallic glass thin films represent promising coatings in the biomedical sector for their combination of antibacterial property and wear resistance. However, finding a Zr-Cu metallic glass composition with desirable cytocompatibility and antibacterial property is extremely challenging. In this work, we have created a cytocompatible and (super-)hydrophobic Zr-Cu-Ag metallic glass coating with ≈ 95% antifouling properties. First, a range of different chemical compositions were prepared via Physical Vapor Deposition magnetron by co-sputtering Zr, Cu, and Ag onto a Polybutylene terephthalate (PBT) substrate among which $Zr_{93.5}Cu_{6.2}Ag_{0.2}$, $Zr_{76.7}Cu_{22.7}Ag_{0.5}$, and $Zr_{69.3}Cu_{30.1}Ag_{0.6}$ were selected to be further investigate for their surface properties, antibacterial activity, and cytocompatibility. SEM images revealed a micro-roughness fibrous structure holding superhydrophobic properties demonstrated by specimens' contact angle measurements ranging from 130° to 150°. To distinguish between antifouling and bactericidal effect of the coating, ions release from coatings into LB and DMEM solutions were evaluated by ICP-MS measurements after 1day and 5 days. Antifouling properties were evaluated by infecting specimens' surface with the Gram-positive *Staphylococcus aureus* and the Gram-negative *Escherichia coli* strain. Results were visually confirmed by FESEM and fluorescent live/dead staining. Human mesenchymal stem cells were used for direct cytocompatibility evaluation of coated samples and their metabolic activity was evaluated via relative fluorescence unit after 24 hours and 5 days. The results were further visualized by FESEM, Fluorescent staining by Live/Dead Viability/Cytotoxicity Kit and confirmed the cytocompatibity of all coated samples. Finally, BhMSC' cytoplasm was stained by May Grunwald and Giemsa after 5days to detect and visualize the released ions which have diffused through the cells membrane.

Keywords: metallic glass; coating; superhydrophobic; antifouling; antibacterial textile.

NanoMed 2021 Onsite Session I

Stimuli-responsive hybrid nanoconstructs for efficient theranostic applications in nanomedicine

V. Cauda
Department of Applied Science and Technology, Politecnico di Torino, Italy
valentina.cauda@polito.it

Abstract:

The role of nanomedicine in the figth of cancer is increasing steadly, as cancer itself is still the second major death cause worldwide, even superior to Covid-19 related deaths. Therefore, many investigations related to the role of nanomaterials in biological fluids, their drug adsorption capability towards development of smart drug delivery systems, as well as their ability to respond to intrinsic cues or external stimulations for exploiting therapeutic or imaging purposes are hot topics.

In this lecture, the role of nanomaterials, expecially metal oxide nanoparticles and nanocrystals, in terms of biological identity and strategies to improve their biocompatible and even biomimetic properties will be thoroughly discussed. Surface modifications as well as doping with transition metals on metal oxide nanomaterials will be shown to exploit intriguing properties, able to respond to stimuli activations, such as magnetic fields, light or ultrasound irradiations. These remote activation enables their use as nano-sized contrast agents for high-resolution and site-selective imaging or to develop a toxic action against selected cancer cell in terms of anticancer therapy.

Finally, strategies to impart a selectivity towards cancer cells is proposed, as site-slective targeting with functional moieties and proteins.

References:

1. L. Racca, V. Cauda (2021) Remotely-activated nanoparticles for anticancer therapy" *Nano-Micro Letters*, 13 (11), 1-34.
2. M. Canta, V. Cauda (2020) The investigation of the parameters affecting the ZnO nanoparticles cytotoxicity behaviour: a tutorial review *Biomater. Sci.* 8, 6157 – 6174.
3. S. Villata, M. Canta, V. Cauda (2020) EVs and Bioengineering: From Cellular Products to Engineered Nanomachines *Int. J. Molecul. Sci.*, 21(17), 6048.
4. V. Cauda (2020) Multimodal hybrid and theranostic nanoparticles as smart Trojan horses to fight cancer *Project Repository Journal,* 6, 108–110.
5. L. Racca, T. Limongi, V. Vighetto, B. Dumontel, A. Ancona, M. Canta, G. Canavese, N. Garino, V. Cauda (2020) Zinc Oxide nanocrystals and high-energy shock waves: a new synergy for the treatment, *Frontiers Bioeng. Biotechnol.* 8, 577.

Acknowledgments

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 678151—Project Acronym 'TROJANANOHORSE'—ERC Starting Grant and grant agreement no. 957563—Project Acronym 'XtraUS'—ERC Proof of Concept Grant) and under a Marie Skłodowska–Curie Actions grant (Standard European Individual Fellowships, H2020-MSCA-IF-2018, Grant Agreement No. 842964, Project Acronym "MINT").

Labs, Cells and Organs on Chip

A.van den Berg
BIOS Group/MESA+ Institute – University of Twente, Enschede, The Netherlands

Abstract:
The recent rapid developments in bionanotech and micro/nanofluidic technologies has enabled the realization of miniaturized laboratories. These Labs-on-a-Chip will play an important role in future medicine, both in point-of-care devices for drug or biomarker monitoring, as well as in early diagnostic devices. We developed a pre-filled ready-to-use capillary electrophoresis platform for measuring ions in blood. It is used to monitor lithium in finger-prick blood of manic-depressive patients, but can also be used for measuring calcium in blood for prevention of milk fever, or for measuring creatinine in blood or sodium in urine for early detection of ESRD. Microfluidics can also be exploited to manipulate and experiment with cells on chip. We have developed a microsystem for sperm analysis and selection for artificial insemination, where we can electrically detect and sort healthy sperm cells. Using microdevices we have been able to electroporate and transfect genes into individual cells, and a microdroplet platform was used for encapsulation of single cells in microdroplets, ordering of these microdroplets and 1:1 fusion of these droplets to form hybridomas. Apart from diagnostic and cell manipulation devices, microfluidic devices are increasingly used to realise advanced disease and organ-models, as illustrated by the blood-brain barrier chip and a blood vessel on a chip to study atherosclerosis. These Organs on Chip may lead to more rapid and cheaper drug development, personalised medicine and improved disease models, while minimizing or even eliminating animal testing (3R principle). We have developed a Translational Organ on Chip Platform (TOP) that enables simple plug and play connection of different Organ on Chip modules to a fluidic base plate.

Keywords: Lab on Chip, Organ on Chip, Microfluidics, cells on chip, sensors, Blood Brain Barrier, biomedical applications.

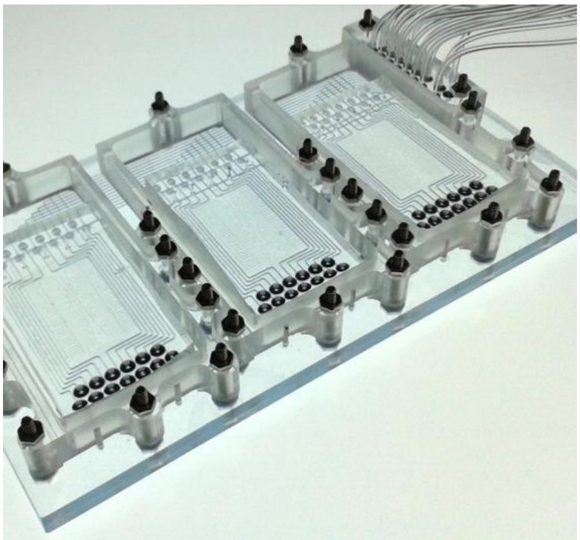


Figure 1:. Microfluidic baseplate for organ on chip modules containing 64 microchambers

References

1. Advanced in vitro models of vascular biology: Human induced pluripotent stem cells and organ-on-chip technology, A Cochrane, HJ Albers, R Passier, CL Mummery, A Van Den Berg, *Advanced drug delivery reviews* **140**, 68-77.

Graphene-based scaffolds towards the treatment of spinal cord injuries

P.A.A.P. Marques[1], N. Barroca[1], A. Girão[1, 6], D. Silva[1], S. Pinto[1], M.T, Portolés[2], M. Cicuéndez[2], R. Diez-Orejas[2], L. Casarrubios[2], M.J. Feito[2], F. Argimiro[3], I. Madarieta[3], N. Garcia-Urkia[3], O. Murua[3], B. Olalde[3], L. Papadimitriou[4], K. Karali[4], E. Stratakis[4], A. Ranella[4], K. Verstappen[5], A. Klymov[5], M.C. Serrano[6]

[1]TEMA, Department of Mechanical Engineering, University of Aveiro, Aveiro, 3810-193, Portugal; [2]Universidad Complutense de Madrid, IdISSC, CIBER-BBN, 28040-Madrid, Spain; [3]Tecnalia Basque Research and Technology Alliance (BRTA), E20009 Donostia-San Sebastian, Spain; [4]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (FORTH/IESL); [5]Regenerative Biomaterials, Radboud University Medical Center, Nijmegen, The Netherlands; [6] Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid 28049, Spain.

Abstract:

Biomedical engineers working in the field of neural tissue engineering have taken notice of graphene-based materials (GBMs) with the goal of harnessing their potential to treat spinal cord injuries (SCI) [1, 2]. The interest of GBM in biomedical engineering comes from their superior biological, electrical, optical, and thermal properties, which together surpass those of commonly used biomaterials, opening up a plethora of unforeseen applications.

The combination of GBMs and natural or synthetic polymers enables the fabrication of three-dimensional scaffolds using various processing techniques, from electrospinning to hydrogel formation and freeze-drying. We have demonstrated that this is a viable and flexible combination for enhancing biomimetic topographical cues with appropriate biological, electrical, and/or mechanical characteristics, therefore improving scaffold properties [3]. Moreover, we have been investigating the effect of adding GBMs, namely graphene oxide (GO) and its reduced counterpart (rGO), to an adipose tissue decellularized matrix (adECM), which contains over 139 proteins and five distinct types of collagen, some of which have been proven to promote neural regeneration, in the context of the FETOPEN project NeuroStimSpinal.

In light of the complexity of the SCI environment, the performance of the scaffolds has been investigated with the major players for the spinal cord to regenerate at the cellular level. When proinflammatory macrophages (M1-like) are present in the spinal cord, a secondary damage process exacerbates the severity of the injury. We have discovered that adECM promotes macrophage polarization toward the reparative M2 phenotype, which has been shown to aid in wound healing following spinal cord damage [4]. Additionally, we demonstrate that GO reduction lowers oxidative stress and the generation of pro-inflammatory cytokines [5], which corroborates our findings. Another critical aspect of the process is avoiding the development of glial scars during spinal cord regeneration. We examined the astrocyte cell response using adECM scaffolds with or without GO, focusing on the expression of reactivity and scar formation-associated genes. When GO was added to the adECM, it led to a significant decrease in the expression of genes involved in scar formation. Additionally, the scaffolds were shown to be excellent platforms for neural stem cell adhesion, survival, and proliferation, with rGO clearly promoting the development of functional neuronal networks, as indicated by neural stem cells differentiation toward neurons and increased synaptophysin expression in the presence of rGO.

Keywords: 3D scaffolds, adipose tissue decellularized matrix, graphene, graphene oxide, neural stem cells, spinal cord injury.

Aknowledgments: EU H2020 research and innovation programme under grant agreement No 829060 (NeuroStimSpinal). UIDB/00481/2020 and UIDP/00481/2020 - FCT - Fundação para a Ciencia e a Tecnologia; and CENTRO-01-0145-FEDER-022083

References:

1. Magaz, A. *et al*, Mater Sci Eng: C 119 (2021) 111632.
2. Girão A.F., *et al*. Biomat Sci 7 (2019) 1228–1239.
3. Girão A.F., *et al*. ACS Appl Mater Interfaces 12 (2020) 38962.
4. Cicuéndez, M. *et al*, Int. J. Mol. Sci. 22 (2021) 3847.
5. Cicuéndez, M. *et al*, Int. J. Mol. Sci. 22 (2021) 6701.

Porous Silicon-Based Microarray Platforms with Carbon Dots Functionalization for Enhanced Viral Detection

L. Gogianu[1], M.A. Popescu[1], A. Radoi[1], A. Sălceanu[1], A. Boldeiu[1], G. Craciun[1], M. Simion[1]

[1] National Institute for Research and Development in Microtechnologies – IMT Bucharest, 126A Erou Iancu Nicolae Street, 077190, Bucharest, Romania
*E-mail: larisa.gogianu@imt.ro

Abstract:
The three-dimensional (3D) configuration of microarray substrates gives better performance than the traditional glass and silicon-based surfaces in terms of higher probe binding capacity and improved hybridization yield [1,2].
The unique morphological, electrical, optical, and mechanical properties of carbon based nanomaterials recommend them for biomedical applications [3,4]. Here, we explored how the localized addition of carbon dots (CDs) on porous silicon (pSi) can potentially enhance the fluorescent signal of the DNA hybridization response in microarrays.
The porous silicon substrate improves the attachment of single-stranded (ssDNA) probes and increases the hybridization yield. Going further, the enhancement of the fluorescent signal is owed to the carbon dots co-immobilized with the ssDNA probes. **Figure 1** presents the hybridization results with HPV 16 amplicon obtained by assymetric PCR. The results are shown for pSi coated with two different SU-8 layer thicknesses.

Keywords: porous silicon, carbon dots, microarray, Human Papilloma Virus, DNA hybridization.

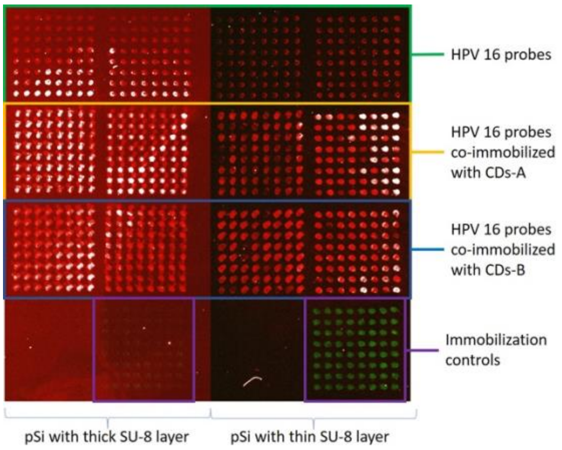


Figure 1: Figure illustrating the hybridization results with HPV 16 amplicons obtained by assymetric PCR. The results are obtained on pSi coated with two SU-8 layer thicknesses. The microarray was achieved using the same laser power.

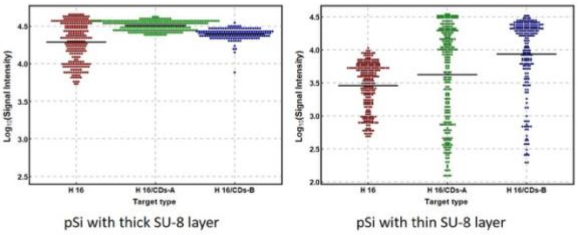


Figure 2 shows the graphical analyses corresponding to the HPV 16 hybridized with the a) ssDNA probes, b) ssDNA probes co-immobilized with CDs-A and c) ssDNA probes co-immobilized with CDs-B.

References:

1. RSC Adv Bouchloukh, W., Jouenne, B. (2012) Characterization of biofilms formation in urinary catheters, *Amer. J. Infect. Control.*, In Press.
2. Talanta Montoneri, F., Montoneri, E., Boffa, V., Sharts, O. (2011), Protein helical structure enhancement in fluorinated-phosphonate nanoporous silica glasses characterized by circular dichroism spectroscopy, *Int. J. Nanotech.*, 8, 471-491.
3. Liu, J., Li, R., Yang, B. (2020), Carbon Dots: A New Type of Carbon-Based Nanomaterial with Wide Applications, *ACS Cent. Sci.* 6, 2179–2195.
4. Mihalache, I. et al. (2015), Charge and energy transfer interplay in hybrid sensitized solar cells mediated by graphene quantum dots, *Electrochim. Acta*, 153, 306–315.

Production and characterization of dual-stimuli nanofibrous membranes

Adriana Gonçalves[1], Filipe Veiga Almeida[1], João Paulo Borges[1], Paula I. P. Soares[1]
[1] CENIMAT | i3N, Department of Materials Science, Caparica, Portugal

Abstract:
Cancer is one of the main causes of death worldwide and its occurrence has been increasing over the years. Due to the therapeutic inefficiency and severe side effects of conventional cancer treatments, the development of new cancer treatment options has been one of the most studied research areas. The development of new multifunctional systems that deliver therapeutic agents locally to the tumor site allows a more personalized and effective treatment. The present work focuses on the development a dual-stimuli responsive device composed of iron oxide magnetic nanoparticles (mNPs) and poly (N-isopropyl acrylamide) (PNIPAAm) microgels embedded in electrospun polymeric fibers capable of providing a simultaneous and local combinatory cancer treatment: chemotherapy and magnetic hyperthermia. The incorporation of microgels and nanoparticles in electrospun nanofibers allows the localization of these systems in the tumor region in a sufficient concentration to enable a more effective treatment [1].

Fe_3O_4 nanoparticles with an average diameter of 8 nm were obtained by chemical precipitation technique and later stabilized with dimercaptosuccinic acid (DMSA) and oleic acid (OA) [2]. PNIPAAm microgels were synthesized by surfactant-free emulsion polymerization (SFEP) [3]. At room temperature, the microgels are in a swollen state, with a hydrodynamic diameter of around 1 μm and above 32 ºC this diameter decreases. At higher temperatures the collapsed state of the microgels takes place, confirming their negative temperature response and Lower Critical Solution Temperature [4]. Poly(vinyl alcohol) (PVA) was used as fiber template and a fiber diameter of 179 ± 14 nm was obtained. 10 wt. % of PNIPAAm microgels and 8 and 10 wt. % of mNPs were incorporated in the PVA nanofibers through colloidal electrospinning technique to produce dual-stimuli nanofibrous membranes. A bead-on-a-string morphology was observed, as shown in Figure 1.

Stress tests of the membranes show that the incorporation of PNIPAAm microgels and iron oxide nanoparticles in the electrospun fibers increases their Young's modulus. Swelling assays indicate PVA membranes have a swelling ratio of around 3.4 and that the presence of microgels in the membrane does not affect its swelling ability. However, with the incorporation of magnetic nanoparticles, the swelling ratio of the membranes decreases. Preliminary contact angle assays demonstrate that PVA MG membranes are slightly more hydrophobic when heated to temperatures above the LCST of PNIPAAm. Magnetic hyperthermia assays show that a higher concentration of nanoparticles leads to a higher heating ability. The composite membrane with the most promising results is the one incorporated with DMSA coated mNPs, since it shows the highest temperature variation, 5.1 ºC. If we consider a body temperature of 37 ºC, a temperature variation of 5.1 ºC is enough to reach the desired 42 ºC in magnetic hyperthermia treatment making this membrane a viable option in cancer treatment. In order to evaluate the cytotoxic effect of PNIPAAm microgels and mNPs incorporated in PVA membranes, cytotoxicity assays were performed. All assays reveal that PVA membranes incorporated with PNIPAAm microgels and mNPs do not present any type of cytotoxicity and therefore can be used in biomedical applications.

A dual-stimuli responsive system was successfully developed. The present work demonstrates the potential of using dual-stimuli composite membranes for magnetic hyperthermia and may in future be used as an alternative cancer treatment. In addition, the developed system also presents a special interest in drug delivery applications in which the device can be remotely triggered by an external stimulus like temperature variation. Drug delivery assays will be performed in the future.

Keywords: colloidal electrospinning, thermoresponsive microgels, magnetic nanoparticles, magnetic hyperthermia, poly (N-isopropyl acrylamide), poly (vinyl alcohol).

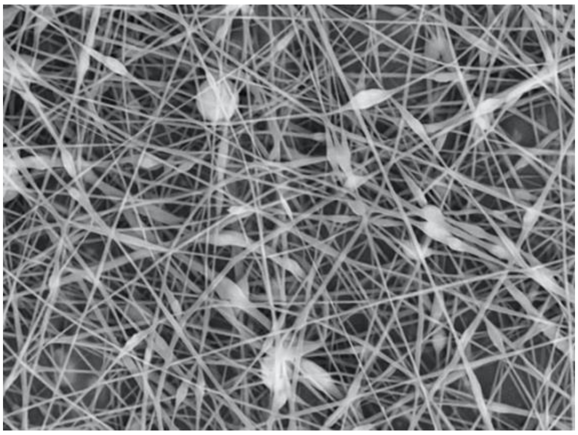


Figure 1: SEM image of PVA nanofibers incorporated with 10 wt. % PNIPAAm microgels and 8 wt.% OA coated mNPs

References:

[1] A. Gonçalves et al. (2021) “Incorporation of Dual-Stimuli Responsive Microgels in Nanofibrous Membranes for Cancer Treatment by Magnetic Hyperthermia,” *Gels*, vol. 7, no. 28.

[2] P. I. P. Soares et al. (2014) “Effects of surfactants on the magnetic properties of iron oxide colloids,” J. C*olloid Interface Sci.*, vol. 419, pp. 46–51.

[3] C. Echeverria et al. (2015) “One-pot synthesis of dual-stimuli responsive hybrid PNIPAAm-chitosan microgels,” *Mater. Des.*, vol. 86, pp. 745–751

[4] M. A. Ward and T. K. Georgiou (2011) “Thermoresponsive Polymers for Biomedical Applications,” *Polymers (Basel).*, vol. 3, no. 3, pp. 1215–1242.

Erythrocytes based carriers for therapy and diagnostic

Giulia Della Pelle[1], Nina Kostevsek[1]

[1]Department for Nanostructured Materials (K7), Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Sloveni

Abstract:

Since the breakout of nanotechnology, health sciences followed the trend. Therefore, in lieu of traditional drug in free form, nanoencapsulation has established as the most promising approach in current pharmacology, since it opens, also, the theranostic formulations (containing diagnostic and reporting/diagnostic agents). Whereas liposomes, micelles and viruses figure as the nanodrugs with highest approval trends, urgency of alternative choices is compelling. This is due to unexpected allergies, immune system recognition and clearance. An alternative is represented by Erythrocytes Membrane Vesicles (EMVs), originated from erythrocytes ghosts. Having CD47 marker on their membrane, which acts as a “don’t eat me!” flag for macrophages, EMVs can have much longer residency in blood than conventional PEGylated stealth liposomes. Such carriers are able to embed superparamagnetic iron oxide nanoparticles (SPION), contrast agents for magnetic resonance imaging, conferring them higher *r2* relaxivity times [1]; also, they are able to prevent photo and thermal degradation of cyanine dyes, used for NIR imaging [2] while retaining therapeutic effect. We are currently aiming to encapsulate them with gene therapy agents, in order to: 1) avoid immune system recognition and rapid clearance; 2) improve in situ delivery; 3) optimize a 3 in 1 formulation for precision medicine, NIR and MRI imaging.

Carbon dots for nanothermometry and *in vivo* stem cell imaging

K.Polakova[1*], S.Kalytchuk[1], T.Malina[1,2], R. Zboril[1,3]
[1] Department Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute, Palacký University, Olomouc, Czech Republic
[2]Department of Physical Chemistry, Faculty of Science, Palacký University Olomouc, Olomouc, Czech Republic
3 Nanotechnology Centre, Centre of Energy and Environmental Technologies, VŠB−Technical University of Ostrava, Ostrava-Poruba, Czech Republic

Abstract:

Carbon dots (CDs) have gained increasing interest in many fields because of attractive functional properties such as broad-band optical absorption, strong luminescence, superior resistance to photobleaching, high chemical stability, low toxicity, and good biocompatibility. They have promising biological applications in fields such as cellular optical imaging, photoacoustic imaging, photothermal therapy, photodynamic therapy, drug delivery, and biosensing. Temperature affects many cellular processes and varies between cells because of biochemical reactions associated with normal cellular metabolism or responses to external stimuli. Intensity- based and ratiometric thermometry approaches are sensitive to errors arising from changes in probe concentration, excitation power, or a lack of temperature specificity. Such obstacles can be overcome by using luminescence lifetime thermal sensing,. Here, we show that water-soluble N,S-co-doped carbon dots (CDs) exhibit temperature-dependent photoluminescence lifetimes and can serve as highly sensitive and reliable intracellular nanothermometers. N,S-CD thermal sensors also exhibit good water dispersibility, superior photo- and thermostability, extraordinary environment and concentration independence, high storage stability, and reusability−their PL decay curves at temperatures between 15 and 45 °C remained unchanged over seven sequential experiments. In vitro PL lifetime-based temperature sensing performed with human cervical cancer HeLa cells demonstrated the great potential of these nanosensors in biomedicine. Tissue regeneration based on stem cell therapy is one of the most rapidly developing fields of modern medicine. Several properties of human mesenchymal stromal cells (MSCs), such as tropism toward a tumor or injury site, make them promising candidates for regenerative medicine, targeted therapy, or treating injured tissues. However, to fully understand the role of stem cells in therapeutic function, their visualization in vivo is essential. Here, we describe, the use of biocompatible quaternized carbon dots (QCDs) as a novel stem-cell tracking probe for in vivo fluorescence imaging of transplanted human MSCs. By studying the in vitro cytotoxicity, intracellular distribution, and precise uptake mechanism, we showed that QCDs had a high biocompatibility and excellent fluorescence properties after 24 h incubation with MSCs. To demonstrate the in vivo feasibility of the system, QCD-labeled MSCs were transplanted subcutaneously into an immunodeficient mouse and visualized by optical in vivo imaging. The labeled cells were strongly fluorescent, allowing their semi-quantitative detection. Moreover, the homing of intravenously transplanted QCD-labeled MSCs into the solid tumor was clearly shown.

Keywords:carbon dots, nanothermometers, photoluminescence life time sensing, stem cell, imaging, diagnosis,

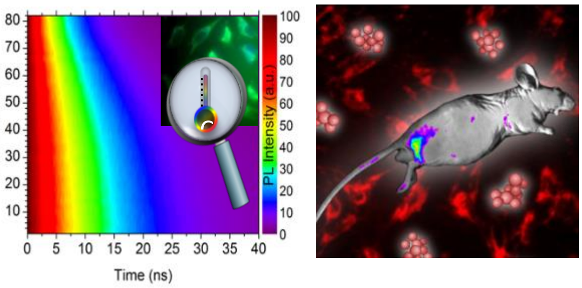


Figure 1: Schema of the bioapplication of carbon dots: The labelled Hela cells by N,S, co-doped CDs as reliable and accurate nanothermometer using PL life time decay (left) and in vivo monitoring of stem cells labelled by red fluorescent carbon dots (right)

References:

1. Kalytchuk, S., Polakova, K. (2017), Carbon Dot Nanothermometry: Intracellular Photoluminescence Lifetime Thermal Sensing, *ACS Nano*,11, 1432-1442.
2. Malina, T., Polakova, K. (2019), Carbon dots for in vivo fluorescence imaging of adipose tissue-derived mesenchymal stromal cells, *Carbon*, 152, 434-443.

Multidrug Delivery Systems Based on Polydopamine Nanoparticles

Klaudia Żebrowska[1,2], Emerson Coy[1], Stefan Jurga[1], Radosław Mrówczyński[3], Bartosz Grześkowiak[1]

[1] NanoBioMedical Centre, Adam Mickiewicz University, Poznań, Poland
[2]Faculty of Physics, Adam Mickiewicz University, Poznań, Poland
[3]Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland

Abstract:
Polydopamine (PDA) has a wide range of applications in biomedicine due to its high biocompatibility. The presence of many functional groups on the surface of PDA enables a very easy modification. It is also possible to cover different types of materials i.e. polymers, ceramics, metals with PDA to improve their properties and stability or to use it as a template for further functionalization. In addition, PDA as a catechol-like material, exhibits excellent chelating properties for binding various types of metal ions, including iron. Big advantage of PDA is wide range of absorption leading to exchange of infrared laser light (808 nm) into heat. That's why PDA is a promising material for cancer treatment with the use of photothermal therapy.[1] There is an urgent need to develop multifunctional nanomaterial which will overcome still escalateing problem of insensitivity or resistance of cancer cells to the drugs. Here we present our ideas of using PDA nanoparticles (NPs) as a carrier for combined multidrug chemo- and photothermal therapy. We obtained two different types of core-shell nanoparticles. Common factors of the synthetized NPs were: PDA, iron ions, PAMAM dendrimers, doxorubicine (DOXO) and curcumin (CUR). Using combination of DOXO with CUR we wanted to investigate the influence of CUR on treatment efficiency.[2] It is known that CUR can be a good support for chemotherapy, because of blocking ABC trasporters which are responsible for DOXO pumping out from the cells, known as MDR effect. Unfortunetly CUR is isolibule in water, that's why it is nessesery to found a porper way to deliver it to cells.[3] In the first type of our nanoparticles, we used PDA as a core and then the surface of NPs was functionalized with iron ions (contrast agent properties in MRI) and PAMAM dendrimer to serve as a container for DOXO and CUR. Second type of nanoparticles was based on CUR crystals core covered with PDA layer. Then, the nanoparticles were similarly functionalized with iron ions and dendrimers. As a resut we present a comprehensive comparision of their physico-chemical and biological properties.

Keywords: polydopamine, iron ions, dendrimers, drug delivery, curcumin, doxorubicine, multidrug resistance, photothermal therapy, biomedical applications.

References:

1. Ball, V. Polydopamine Nanomaterials: Recent Advances in Synthesis Methods and Applications. Front. Bioeng. Biotechnol. 2018, 6 (AUG), 1–12.
2. Zhao, X. et al. Doxorubicin and curcumin co-delivery by lipid nanoparticles for enhanced treatment of diethylnitrosamine-induced hepatocellular carcinoma in mice. Eur. J. Pharm. Biopharm. 93, 27–36 (2015).
3. Pan, H., Shen, X., Tao, W., Chen, S. & Ye, X. Fabrication of Polydopamine-Based Curcumin Nanoparticles for Chemical Stability and pH-Responsive Delivery. J. Agric. Food Chem. 68, 2795–2802 (2020).

Acknowledgements: The financial support under research grant number POWR.03.02.00-00-I032/16 by The National Centre for Research and Development "Środowiskowe interdyscyplinarne studia doktoranckie w zakresie nanotechnologii" under the European Social Fund - Operational Programme Knowledge Education Development is kindly acknowledged.

A novel theranostic agent and nanoparticle drug delivery for Boron Neutron Capture Therapy

Jacopo Sforzi[1], Diego Alberti[1], Rachele Stefania[1], Alberto Lanfranco[2],
Annamaria Deagostino[2], Silvio Aime[1], Simonetta Geninatti Crich[1]

[1]Deparment of Biotechnology and Health Sciences, University of Torino,
via Nizza 52, 10125, Torino, Italy
[2]Department of Chemistry, University of Torino, via P. Giuria 7, 10125, Torino, Italy.

Abstract:
Boron Neutron Capture Therapy (BNCT)⁽¹⁾ is a promising option for tumoral treatment, relying on the selective delivery of boron atoms to cancer cells, followed by the irradiation with a neutron beam of the diseased organ The innovation of this study lies on the development and test of a nanosized theranostic agent, able to maximize the selective uptake of boron atoms in tumor cells and, at the same time, to quantify (by MRI) the in vivo boron biodistribution that is crucial to determine the optimal neutron irradiation time and to calculate the delivered radiation dose.

Methods: In this study we used the theranostic compound AT101⁽²⁾ (10 B enriched ligand-C-[N-(DOTAMA-C6)carbamoylmethyl]C′-palmitamidomethyl-o-carborane), a compound containing a Gd atom for imaging purposes, and 10 Boron atoms organised in a carborane structure for BNCT. AT101 was internalised into PLGA (Poly,(lactic-co-glycolic acid) nanoparticles:these NPs are coated with DSPE-PEG-2000 and produced with and w/o 50% of a PLGA conjugated with a polyhistidine chain(n=15).The NPs were dialysed to remove the unbound AT101 and incubated with mesothelioma (AB-22) and healthy mesothelium cell lines (MET-5α) for 24 h in a petri dish. The cells were collected and sonicated. A portion of each batch was mineralised to analize Gd concentration with ICP-MS ,the remaining portion is used to quantify proteins.

Results: PLGA NPs containing AT101 were characterised using Dynamic Light Scattering, showing an average size of 132±13 nm, with a Polydispersion index never superior to 0.15, suggesting the good quality and reproducibility of the preparations. We observed no significant release of AT-101 from the NPs when incubated for 72 h with Hepes buffer at 37°C and different pH, suggesting a good stability. Two different NPs were created, both containing AT-101 but with or w/o PLGA conjugated with poly-histidine, a feature that is in theory able to swell and alter the charge of the nanoparticle at different pH. They were incubated with AB-22 and MET-5α cell lines. We observed a significant increase in the nanoparticle uptake in AB-22 cell line, compared with MET-5α, and interestingly, in AB-22 cells, the NP containing Poly-his has a double internalisation rate compared to the one w/o the Poly-His feature. The evaluation of the corresponding contrast enhancement in the T1 weighted MR image has confirmed the results obtained in previous experiments, showing an

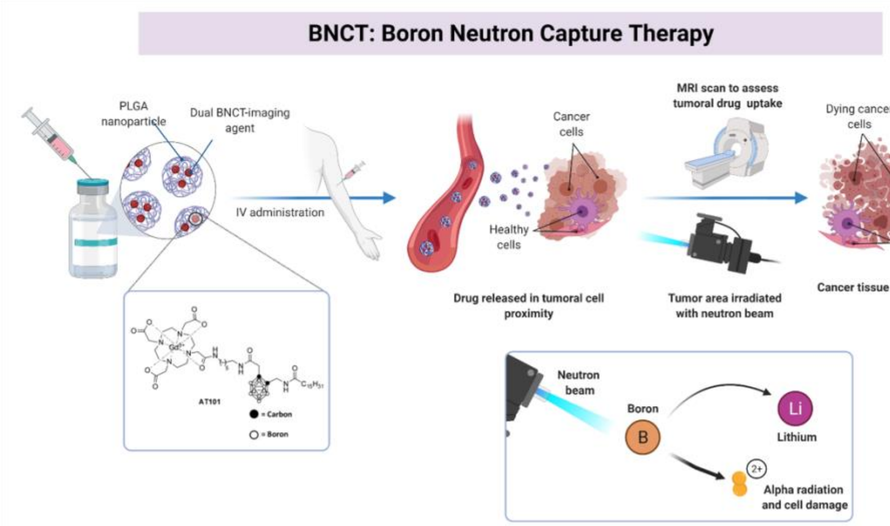


Figure 1: Boron Neutron Capture Therapy Rationale:
PLGA nanoparticles carrying the theranostic agent AT101 are delivered to the patient, interacting selectively with cancer cells. After MRI imaging to assess the drug uptake, the cancer mass is irradiated with a neutron beam; the boron atoms present in the drug then decays into lithium and alpha particles, damaging the cells and therefore the

increased uptake in tumoral cells compared to healthy ones.

Conclusion: This therapy can potentially affect only tumor cells with a lethal dose of radiations, even in case of spreading and infiltrative cases. These promising insights on the possibility to selectively direct a theranostic dual agent directly into tumoral cell, with the possibility to analise the drug uptake in a certain organ using MRI, may be an important, versatile and new starting point for the future of BNCT technology and cancer theranostics.

Keywords: boron neutron capture therapy, BNCT, theranostic drug, nanoparticles, PLGA, drug delivery, MRI, Gadolinium contrast agent, Neutron radiation., Mesothelioma, asbestos, biomedical applications.

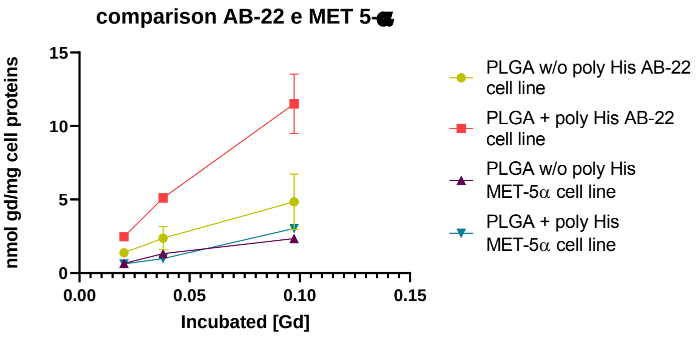


Figure 2: Figure illustrating the selective uptake of PLGA NPs with poly-His coating nanoparticles selectively entering the mesothelioma cell line AB-22, when compared to non-functionalised NPs; furthermore, both the nanoparticles have shown very love intake into healthy mesothelium MET-5α cell line.

References:

1. Dymova, MA, Taskaev, SY, Richter, VA, Kuligina, EV. Boron neutron capture therapy: Current status and future perspectives. Cancer Communications. 2020; 40: 406– 421. https://doi.org/10.1002/cac2.12089

2. S. Geninatti-Crich, D. Alberti, I. Szabo, A. Deagostino, A. Toppino, A. Barge, F. Ballarini, S. Bortolussi, P. Bruschi, N. Protti, S. Stella, S. Altieri, P. Venturello, S. Aime MRI-guided neutron capture therapy by use of a dual gadolinium/boron agent targeted at tumour cells through upregulated low-density lipoprotein transporters Chemistry, 17 (2011), pp. 8479-8486

Remote control of axon outgrowth by magnetic nanoparticles

A. Falconieri [1], S. De Vincentiis [1], S. Figoli [1], S. Ghignoli [1], D. Convertino [2], M. Mainardi [3], V. Cappello [4], L. Marchetti [1], M. Costa [3], V. Raffa [1]

[1] Università Di Pisa, [2] Istituto Italiano di Tecnologia, [3] CNR, [4] Scuola Normale Superiore

Abstract:

Axonal growth mediated by active mechanical stimuli is perhaps the most remarkable mechanism for axonal elongation described so far and axons have been described to elongate at impressive rates [1]. Surprisingly, no practical applications have been proposed yet because of the lack of enabling technologies. Recently, we validate a remotely-actuated (non-invasive) methodology with a translational potential based on magnetic manipulation of axons labelled with magnetic nanoparticles [2,3].

We found in hippocampal neurons that this physical manipulation induces axonal outgrowth. The extreme axon elongation is accompanied by a mass addition as we observed no reduction in axon caliber. We profiled axonal transcriptome via RNAseq and many differentially expressed genes belongs to the functional categories of synapsis (development, maturation, plasticity) and cytoskeleton remodelling. Molecular, ultrastructure and functional studies confirmed extensive remodelling of axonal cytoskeleton and synapsis. Interestingly, our data suggest that a positive modulation of local mechanisms (axonal transport and local translation) would provide the new mass required to sustain this extreme axonal outgrowth.

Keywords: mechanotransduction, axon outgrowth, magnetic nanoparticles

References:

1. De Vincentiis, S., Falconieri, A., Scribano, V., Ghignoli, S., Raffa, V. Manipulation of axonal outgrowth via exogenous low forces.International Journal of Molecular Sciences, 2020, 21(21), pp. 1–27, 8009
2. De Vincentiis, S., Falconieri, A., Mainardi, M., ...Costa, M., Raffa, V. Extremely Low Forces Induce Extreme Axon Growth. Journal of Neuroscience, 2020, 40(26), pp. 4997–5007
3. Raffa V, Falcone F, De Vincentiis S et al. Piconewton Mechanical Forces Promote Neurite Growth. Biophysical journal 115(10), 2026-2033 (2018).

Cutting-edge biofunctionalized nanoparticles: a step toward technological innovation

M. Colombo [1]
[1] NanoBioLab, University of Milano-Bicocca, Department of Biotechnologies and Bioscience,
Milano, Italy

Abstract:
Multifunctional nanoparticles are promising tools for different kinds of applications in medicine. Most of the studies with nanoparticles in medical field focused on the development of new innovative tools. One of the greatest challenges in designing nanoparticles functionalized with bioactive molecules to optimize molecular recognition resides in the possibility to finely control the ligand orientation on the nanoparticle surface (**Figure 1**).

On the other hand, many efforts have been dedicated to the study of different administration routes alternative to the intravenous one. To support the research in new drug delivery nanosystems, in the past few years, I focused my research on the exploration of new innovative approaches for nanoparticle administration that combine the nanoparticle features with the potential of innovative formulations in order to obtain a synergistic effect.

Keywords: colloidal nanoparticles, biofunctionalization, formulation, administration routes

Figure 1: Functionalization of colloidal nanoparticles with a discrete number of ligands. A newly designed recombinant HALO-GFP fusion protein was produced to demonstrate the feasibility of controlling number, orientation and full functionality of protein ligands conjugated onto the surface of colloidal gold nanoparticles via bioclick reaction (1).

References:

1. S. Garbujo, et al. (2020) Functionalization of colloidal nanoparticles with a discrete number of ligands based on a “HALO-bioclick” reaction. *Chem Commun* 56, 11398.
2. Rizzuto, M.A., et al. (2021) H-Ferritin nanoparticle-mediated delivery of antibodies across a BBB in vitro model for treatment of brain malignancies. *Biomat. Scie.* 9, 2032.
3. Rotem, R., et al. (2020) Modeling the interaction of amphiphilic polymer nanoparticles with biomembranes to Guide rational design of drug delivery systems. *Colloid surface B* 196, 111366.
4. L. Salvioni, et al. (2021) The emerging role of nanotechnology in skincare. *Adv Colloid Interfac*, 293, 102437.

The role of colloidal stabilization and pH evolution in mesoporous silica nanoparticles formation: a comprehensive mechanistic study

Viktoriya Semeykina*, Ilya Zharov

viktoriyacatalysis@gmail.com

Department of Chemistry, University of Utah, Salt Lake City, USA

Abstract: Monodisperse mesoporous silica nanoparticles represent a very promising and rapidly developing type of materials, however, the vast data on their synthesis still remains haphazard.[1] We attempted to systematically study the formation of monodisperse nanoparticles under basic conditions using various concentrations of hydrolyzing agents (TEA, ammonia, phosphate buffers) and media with different colloidal stabilization properties (additives of EtOH cosolvent, monovalent M^+X^- salts). A large set of experimental data showed that the traditional classical nucleation theory poorly explains the observed particle size trends. We suggest that colloidal stabilization by the media often determines the particle size and morphology, in addition to the hydrolysis and condensation rates conventionally used for data interpretation. In situ pH measurements showed that the pH evolution throughout the synthesis is significantly affected by the buffer capacity and condensation rates, and failure of the reaction system to maintain basic pH results in the non-porous products or undesired particle morphology and distribution. The data on the particle formation mechanism allowed us to create a comprehensive guideline for the preparation of monodisperse mesoporous silica 30-700 nm spheres with variable porosity (V_{meso} ~ .1-0.5 cm^3/g) and mesopore size (2-20 nm). We suggest facile techniques that produce reasonable amounts of nanoparticles with available and non-toxic reagents. These findings will be especially useful for designing new types of mesoporous silica-containing materials for biomedical applications.

Keywords: mesoporous silica nanoparticles, silica, MSN, drug delivery, synthesis

References:

1. Croissant, J. G., Fatieiev, Y., Almalik, A. & Khashab, N. M.(2018) Mesoporous Silica and Organosilica Nanoparticles: Physical Chemistry, Biosafety, Delivery Strategies, and Biomedical Applications. *Adv. Healthc. Mater.* **7**, 1–75.

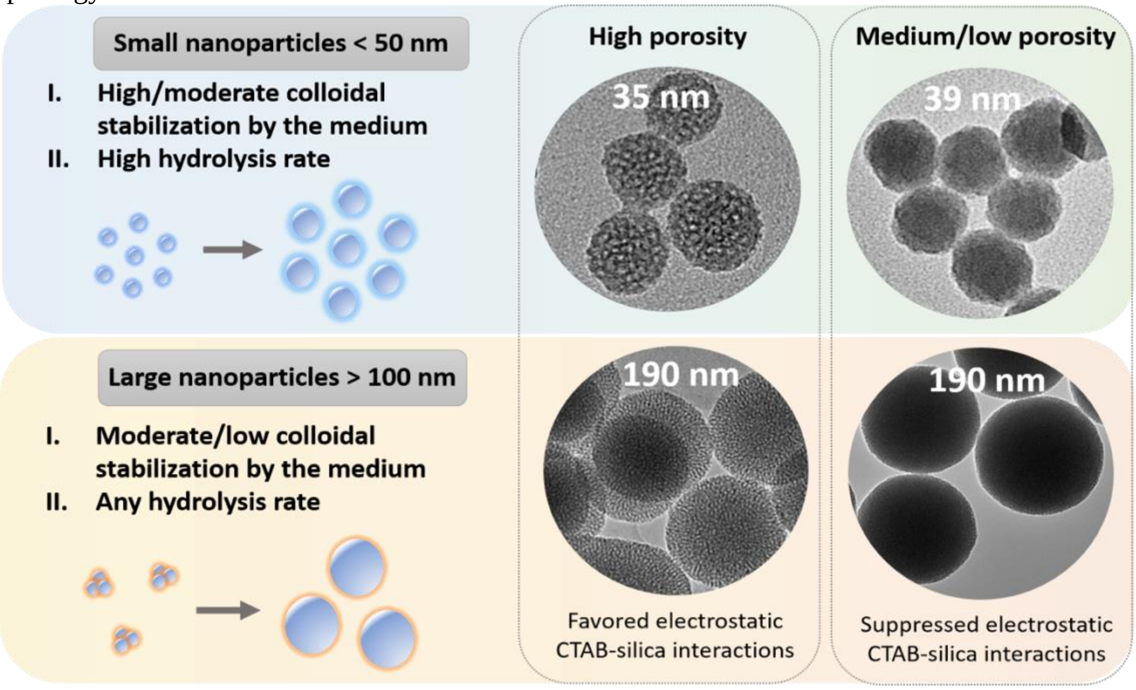


Figure 1. A general scheme illustrating the formation of mesoporous silica nanoparticles with various sizes and porosities.

Covalent Chitosan-Polyethylenimine Derivatives as Gene Delivery Vehicles

L. Nicolle [1*], C.M.A. Journot [1], P. Robin [1], J. Casper [2], P. Detampel [2], M. Williman [3], H.-M. Grisch-Chan [3], T. Einfalt [2], B. Thöny [3], J. Huwyler [2], S. Gerber-Lemaire [1]

[1] Group for Functionalized Biomaterials, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
[2] Division of Pharmaceutical Technology, Department of Pharmaceutical Sciences, University of Basel, Basel, Switzerland
[3] Division of Metabolism and Children's Research Center, University Children's Hospital Zürich, Zürich, Switzerland

Abstract:

There is an increasing interest in cationic polymers as important constituents of non-viral gene delivery vectors. Among them, chitosan (CS) is a promising polymeric backbone due to its biocompatibility, biodegradability and versatility towards functionalization. This project aims to develop a CS-based gene delivery vehicle for liver-targeted diseases. In order to ensure optimal biological applications, the CS backbone was first depolymerized through a microwave-assisted controlled degradation method, leading to water-soluble chains (dCS; 6–9 kDa).[1] Low molecular weight linear polyethylenimine (LPEI; 2.5 kDa) was then covalently grafted on the dCS backbone and the resulting conjugates were analyzed for their physico-chemical properties, before being assessed *in vitro* and *in vivo* for gene delivery applications.[2] We identified a lead dCS-LPEI derivative which showed a 10-fold higher transfection signal in wild-type mice when compared to the commercially available non-viral delivery vector *in vivo*-jetPEI. This promising non-viral gene delivery system is now further investigated for additional covalent derivatization with heterobifunctional polyethylene glycol chains (PEG; 2 kDa and 0.4 kDa), cell-penetrating peptides (CPP), fluorophores and hepatocyte-targeting ligands (Figure 1). We expect to improve the copolymer's biocompatibility by taking advantage of the shielding effect of PEG. Then, the transfection efficiency shall be increased thanks to the addition of a CPP and a targeting ligand. Finally, the cross reactive PEG chains will provide further stabilization of the polymeric vehicle *via* cross-linking between the different chain ends. Fluorescent labelling was also implemented to allow more in-depth study of the DNA delivery mechanism occuring both *in vitro* and *in vivo* with such system. We herein disclose the results on the functionalization of dCS-LPEI system, including physico-chemical characterization, *in vitro* evaluation and *in vivo* studies.

Keywords: chitosan; polyethylenimine; covalent conjugation; copolymer; gene delivery vector.

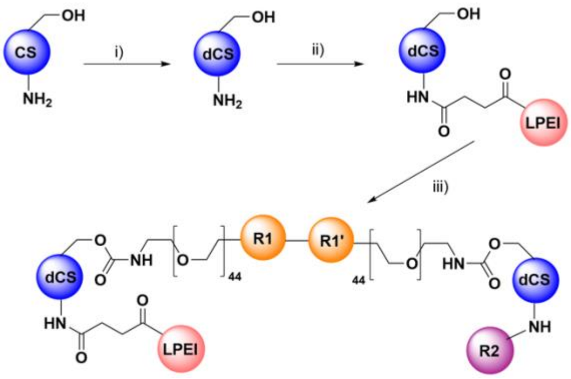


Figure 1: Synthetic pathway toward multi-functional polymeric gene delivery vehicle. i) CS depolymerization *via* microwave-assisted depolymerization method. ii) Grafting of LPEI on dCS using a succinyl linker. iii) Derivatization of the initial dCS-LPEI system with heterobifunctional PEG, CPP, fluorophore and hepatocyte-targeting ligand. R1, R1' = maleimide, thiol, and acrylate functionalities. R2 = CPP, fluorophore or targeting ligand.

References:

1. Journot, C.M.A., Nicolle, L., Lavanchy, Y., Gerber-Lemaire, S. (2020) Selection of water-soluble chitosan by microwave-assisted degradation and pH-controlled precipitation, *Polymers*, 12, 1274.
2. Nicolle, L., Casper, J., Willimann, M., Journot, C.M.A., Detampel, P., Einfalt, T., Grisch-Chan, H.M., Thöny, B., Gerber-Lemaire, S., Huwyler, J. (2021) Development of covalent chitosan-polyethylenimine derivatives as gene delivery vehicle: synthesis, characterization, and evaluation, *Int. J. Mol. Sci.*, 22, 3828.

Novel hybrid nanoparticles for Alzheimer's disease theranostic: efficient overcoming of nanomaterials across the blood-brain-barrier

C. I. P. Chaparro [1,2], V. Neves [2], J.P. Borges [1], P. I. P. Soares [1]

[1] CENIMAT/I3N, Materials Science Department, Nova University of Lisbon, Almada, Portugal
[2] Instituto de Medicina Molecular, Faculty of Medicine, University of Lisbon, Lisboa, Portugal

Abstract:
Alzheimer's disease (AD) is a chronic and progressive brain disease that leads to deterioration of cognitive function [1]. The distinguishing pathological hallmark of AD is the build-up of cortical and cerebrovascular deposits of amyloid-β (Aβ) peptide. Development of novel nanomaterials as imaging contrast agents and drug delivery systems for early detection and treatment of AD, is a recent and promising strategy [2].

Nanotechnology-based approaches such as nanoparticles (NPs), have provided enormous hope by overcoming issues regarding poor BBB permeability and drug delivery applications. Magnetic nanoparticles (MNPs) have become an appealing strategy for AD theranostic since they can act as a multifunctional platform. Superparamagnetic iron oxide nanoparticles (SPIONs) are particularly used as contrast agents for magnetic resonance image (MRI), as cell labelling agents for cell tracking and to induce magnetic hyperthermia (MH) [3]. Polymer's biodegradability facilitates clearance of the nanocarrier and can be exploited to trigger drug release. Poly(lactic-co-glycolic) acid (PLGA) nanoparticles enhance drug pharmacodynamic and bioavailability and, in the present work they are used to incorporate magnetic cores within their nanostructure.

The present study aimed to develop a nanoparticulate system that translocate the BBB and actively target Aβ peptides to promote their disaggregation. The work comprises the conjugation of a peptide that reversibly crosses the BBB (PepH3) [4], with a tailored antibody fragment for Aβ, which allows clearance of the toxic Aβ from the brain to the blood [5].

SPIONs were synthesized by thermal decomposition technique with an average core diameter of 6 nm and superparamagnetic behavior confirmed by TEM and SQUID techniques, respectively. PLGA-NPs were simultaneously prepared with stabilized SPIONs through simple-emulsion solvent evaporation technique to allow SPIONs encapsulation. After encapsulation process, the formulations tested in this work were within the size range of 212–340 nm (Figure 1). The iron content of SPIONs was determined using 1,10-phenanthroline colorimetric method through UV/VIS spectrometry. Encapsulation efficiency (EE) values fluctuate between 30 and 90% and are directly related with SPIONs concentration, PLGA mass and surfactant agents' concentration. The sizes of nanoparticles are as well dependent on these features. Magnetic hyperthermia studies suggest that both formulations with higher SPIONs EE values are capable of increase their temperature of up to 7ºC. To improve the therapeutic effectiveness in AD the construct VL2-PepH3 is being conjugated to nanoparticles' surface. Both functionalization process and stability studies of formulations are being tested for further *in vitro* assays which comprises translocation across the BBB model and its integrity assessment. To carry out these procedures, we intend to test the BBB interaction with the developed nanosystem using a BBB *in vitro* model.

Keywords: Magnetic nanoparticles, polymeric nanoparticles, biomaterials for magnetic stimulation, cell-particles interactions, blood-brain-barrier, Alzheimer's disease, biomedical applications.

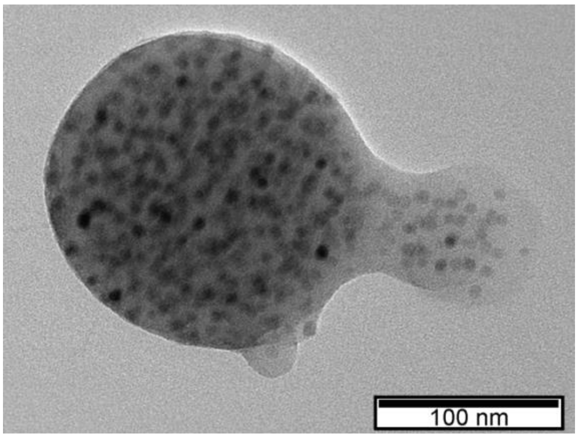


Figure 1: TEM image of iron oxide nanoparticles (black spots) encapsulated in a PLGA nanoparticle.

References:

1. Furtado, D., Björnmalm, M., Ayton, S., Bush, A. I., Kempe, K., Caruso, F. (2018), Overcoming the Blood–Brain Barrier: The Role of Nanomaterials in Treating Neurological Diseases, *Adv. Mater.*, 30(46).
2. Dilnawaz, F., Sahoo, S. K. (2015), Therapeutic approaches of magnetic nanoparticles for the central nervous system, *Drug Discov. Today*, 20(10), 1256–1264.
3. Chaparro, C. I. P., Loureiro, L. R., Valente, M. A., Videira, P. A., Borges, J. P., Soares, P. I. P. (2019), Application of Hyperthermia for Cancer Treatment: Synthesis and Characterization of Magnetic Nanoparticles and their internalization on Tumor Cell Lines*, *2019 IEEE 6th Portuguese Meeting on Bioengineering (ENBENG)*.
4. Neves, V., Aires-da-Silva, F., Morais, M., Gano, L., Ribeiro, E., Pinto, A., Aguiar, S., Gaspar, D., Fernandes, C., Correia, J.D.G., Castanho, M. (2017), Novel Peptides Derived from Dengue Virus Capsid Protein Translocate Reversibly the Blood-Brain Barrier through a Receptor-Free Mechanism. *ACS Chem Biol.*,12(5),1257-1268.
5. Côrte-Real, S., Neves, V., Oliveira, S., Canhão, P., Outeiro, T., Castanho, M., Aires da Silva, F. (2016), Antibody Molecules And Peptide Delivery Systems For Use In Alzheimer's Disease And Related Disorders. International, WO2016120843A1 WIPO (PCT) wo/2016/120843.

Modulation of lipid metabolism in brain cells using poly-ion complex micelles containing CoA-conjugated CPT1A inhibitors

W. Paraiso[1], J. Garcia-Chica[2,3,4], X. Ariza[3,5], S. Zagmutt[2], S. Fukushima[1], J. Garcia[3,5], Y. Mochida[1], D. Serra[4,5], L. Herrero[4,5], H. Kinoh[1], N. Casals[2,5], K. Kataoka[1], R. Rodríguez-Rodríguez[2], and S. Quader[1]
[1]Innovation Center of Nanomedicine, Kawasaki Institute of Industrial Promotion, Japan
[2]Faculty of Medicine and Health Sciences, Universitat Internacional de Catalunya, Spain
[3]Faculty of Chemistry, Universitat de Barcelona, Spain
[4]School of Pharmacy and Food Sciences, Universitat de Barcelona, Spain
[5]Centro de Investigación Biomédica en Red de Fisiopatología de la Obesidad y la Nutrición (CIBEROBN), Instituto de Salud Carlos III, Spain

Abstract:

Carnitine palmitoyltransferase 1A (CPT1A), which catalyzes the first committed step to fatty acid oxidation (FAO), is a central player in lipid metabolism. Inhibiting this enzyme in the brain is linked to several pharmacological benefits [1]. One strong competitive inhibitor to CPT1A is C75-CoA. However, it has low cellular permeability because of its anionic charge. We report the use of poly-ion complex (PIC) micelles to deliver the CPT1A inhibitors, (±)-, (+)-, and (–)-C75-CoA into U87MG glioma and GT1-7 neurons [2] (Figure 1).

PIC micelle formation was made possible by charge-neutralization of the cargo with the protonated amine side chain of PEG-poly{*N*-[*N'*-(2-aminoethyl)-2-aminoethyl]aspartamide} (PEG-PAsp(DET)), resulting in particles with 55 to 65-nm diameter. Upon short-term incubation with cells, the micelle-encapsulated CPT1A inhibitors resulted in up to 5-fold reduction of ATP synthesis, compared with the free drug. C75-CoA micelle treatment showed a discernible decrease in ^{14}C-palmitate oxidation into CO_2 and acid-soluble metabolites, verifying that the substantial decrease in ATP synthesis was related to FAO inhibition. Incubation of cells with the PIC micelles also resulted in increased cytotoxicity to glioma cells, as shown when IC_{50} was diminished by 2 to 4-fold over the free drug-treated U87MG after long-term incubation. For cellular uptake measurement of these CoA-adduct loaded PIC micelles, we synthesized a fluorescent CoA adduct and prepared Fluor-CoA micelle which showed effective internalization in both cell lines in 2D and 3D culture models, especially in neurons where uptake reached up to 3-fold over the free dye.

Our results strongly demonstrate that uptake in neuronal and glioma cells of small anionic cargoes like Fluor-CoA and by extension, C75-CoA, is thoroughly improved by using a PIC micelle. Additionally, the advantage of using a micelle-type delivery system was more pronounced for the neurons as compared to the glioma cells, in which is generally more challenging compared to other cells [3]. These findings contribute to the growing pool of knowledge on glioma- and neuron-targeted delivery, therefore warranting further development into effective brain therapeutics, which especially involve the delivery of negatively-charged molecules for disease therapy.

Keywords: poly-ion complex micelles, obesity, cancer, brain delivery, glioma, neurons

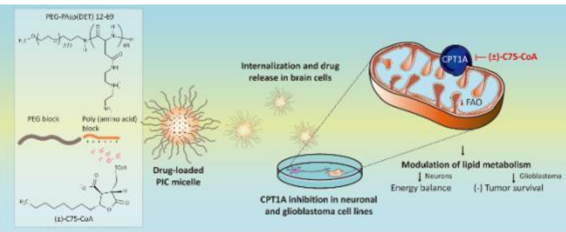


Figure 1: Preparation of (±)-C75-CoA micelle and its effect on lipid metabolism in brain cells

References:

1. Casals N, Zammit V, Herrero L, Fadó R, Rodríguez-Rodríguez R, Serra D. 2016 Carnitine palmitoyltransferase 1C: From cognition to cancer. *Prog. Lipid Res.* **61**, 134–148. (doi:10.1016/j.plipres.2015.11.004)
2. Paraiso WKD *et al.* 2021 Poly-ion complex micelle effectively delivers CoA-conjugated CPT1A inhibitors to modulate lipid metabolism in brain cells. *Biomater. Sci.* (doi:10.1039/D1BM00689D)
3. Garcia-Chica J *et al.* 2020 An overview of nanomedicines for neuron targeting. *Nanomedicine (Lond).* **15**, 1617–1636. (doi:10.2217/nnm-2020-0088)

Development of hybrid carbon nanotubes/gold nanostars for cancer treatment by hyperthermia

Rym Soltani[1], Ali Abou-Hassan,[2] Claire Wilhelm,[3] Alberto Bianco,[1] Cécilia Ménard-Moyon[1]
[1]CNRS UPR 3572, Immunologie, Immunopathologie et Chimie Thérapeutique, ISIS, Université de Strasbourg, Strasbourg, France
[2]Sorbonne Université, CNRS UMR 8234, PHysico-chimie des Electrolytes et Nanosystèmes InterfaciauX (PHENIX), Paris, France
[3]Institut Curie, CNRS UMR 168, Laboratoire Physico-Chimie Curie, Paris, France

Abstract:
The conventional methods for cancer therapy, namely surgery, radiation, and chemotherapy can damage healthy tissues and cause a lot of undesired side effects. Nanotechnology offers remarkable solutions in the field of medicine, especially in early detection and is likely to generate novel and highly effective therapeutic agents. Carbon nanotubes (CNTs) are sp^2 hollow cylindrical molecules made of rolled-up sheet of graphene that show unique physicochemical properties, which make them good candidates for numerous applications in nanomedicine. Gold nanoparticles are characterized by a large surface-enhanced Raman scattering (SERS) activity, excellent photothermal properties and low cytotoxicity. In this context, the aim of this project is to combine multi-walled carbon nanotubes (MWCNTs) with gold nanostars (AuNSs) and study their potential synergistic effect by photothermal therapy (PTT) to induce a selective elimination of cancer cells [1-2]. This method is based on the conversion of absorbed near-infrared light into a local hyperthermia that will destroy the malignant cells and keep the healthy ones safe. Two different types of functionalized MWCNTs were synthesized, both bearing sulfhydryl groups to exploit the affinity of SH groups for gold. To prepare these hybrid carbon nanotube/gold nanostar conjugates, two strategies were investigated: the first is based on the decoration of CNTs with pre-formed AuNSs, while the second consists on the *in situ* growth of AuNSs on the nanotube surface. The conjugates were characterized by UV-Vis-NIR spectroscopy and transmission electron microscopy (TEM) (Figure 1). The efficacy of the different CNT/AuNS conjugates for PTT and their *in vitro* efficiency will also be evaluated. Overall, we expect the hybrid system to be a great photothermal agent able to induce efficient cancer cell ablation.

Keywords: Carbon nanotubes – gold nanostars – cancer therapy – photothermal therapy.

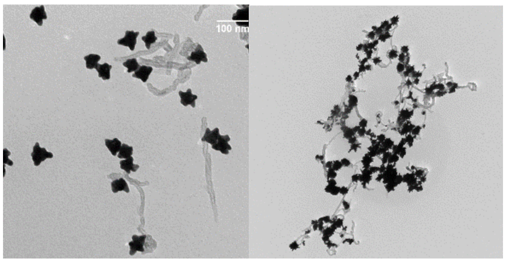


Figure 1: TEM images of CNT/AuNS conjugates.

References:

1. Yang, W., Liang, H., Ma, S., Wang, D., Huang, J. (2019), Gold nanoparticle based photothermal therapy: Development and application for effective cancer treatment, *Sustain. Mater. Technol.*, 22, e00109
2. Jiang, B.-P., Zhou, B., Lin, Z., Liang, H., Shen, X.-C. (2019), Recent advances in carbon nanomaterials for cancer phototherapy, *Chem. Eur. J.*, 25, 3993-4004

Flavin Adenine Dinucleotide (FAD)-Complex Gold Nanoparticles: Chemical Design, Physico-Chemical and assessment therapeutic Effects of FAD on a Breast Cancer Model of Mouse

Celia Arib[1‡], Hui Liu[2‡], Qiqian Liu[1], Anne-Marie Cieutat[1],Didier Paleni[3], Xiaowu Li[2*],Jolanda Spadavecchia[1-2*]

[1] CNRS, UMR 7244, NBD-CSPBAT, Université Sorbonne Paris Nord, campus Bobigny, France
[2] Department of Hepatobiliary Surgery, Guangdong Provincial Key Laboratory of Regional Immunity and Diseases & Carson International Cancer Center，Shenzhen University General Hospital
[3]BioEVEN start-up, 75 rue de Lourmel 75015 Paris

Abstract:
The development of effective drug delivery systems is one of the major challenges in the fight against cancer.Flavoproteins play a key role in regulatory process cell life, they are involved in several redox reactions that regulate the metabolism of carbohydrates, amino acids and lipids. This study was involved in the nanomedicine pathway to encapsulate the cofactor Flavine Adenine Dinucleotide (FAD), using polymeric gold nanoparticles (PEG-AuNPs) through two chemical methods of functionalization (chelation (IN); carbodiimide chemistry (ON)). These hybrid gold nanoparticles and their precursors were characterized by analytical techniques (Raman; UV-Vis, H^1-RMN, Transmission Electron Microscopy (TEM)) which confirmed the grafting of cofactor agent. The main results have been completed by computational studies (Density Functional Theory (DFT)) in agreement with the experimental observations. We also monitored the interaction of our hybrid nanoparticles systems with small aptamers (APT) in order to hypothese the biomolecular mechanism and also to investigate their biological efficacency in pancreatic cancer cells (MIAPaCa-2 cells).

After development of the synthesis, a mouse liver cancer model induced by Hep1-6 cells was used to evaluate the therapeutic efficacy of FAD (named NP1) and FAD-PEG diacide complex (named NP2). The survival time of the tumor-bearing mice, body weight and tumors volume were measured and recorded. The cytokines were used to detect the serum inflammatory factors and the blood cell analyzer was used to determine the blood cell content of different groups of nude mice. The outcomes demonstrate that FAD formulations (NP1; NP2) significantly suppressed the tumor growth and reduce the tumor index without effects on the body weight of mice. Moreover, NP2 significantly reduced the serum levels of cytokines IL-6, TNF-α and IL-12 (P70). The reported results provide the proof-of-concept for the synthesis of a smart adjuvant for liver cancer therapy and support their further development in the field of Nanomedicine.

Keywords: Hybrid gold nanoparticles; Flavine Adenine Dinucleotide (FAD); Raman spectroscopy; UV-visible absorption; DFT; cytotoxicity.

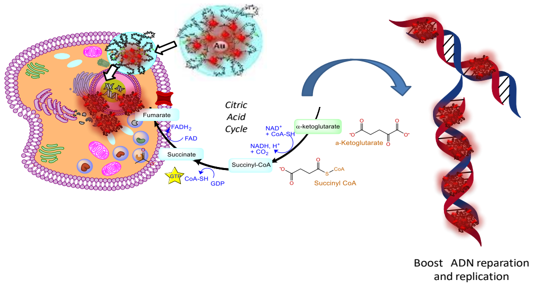


Figure 1: Schematic hypothesis of FAD IN PEG-AuNPs and FAD-PEG DiacideComplex effects on the metabolic and glycolysis pathway in cancer cells.

References:

1. Arib, C., Liu, H., Liu, Q., Cieutat, A. M., Paleni, D., Li, X.,…& Spadavecchia, J. (2021). A Pegylated Flavin Adenine Dinucleotide PEG Complex to Boost Immunogenic and Therapeutic Effects in a Liver Cancer Mo el. Nanotheranostics, 5(4), 405.
2. Moustaoui, H., Movia, D., Dupont, N., Bouchemal, N., Casale, S., Djaker, N., ... & Spadavecchia, J. (2016). Tunable design of gold (III)–doxorubicin complex–pegylated nanocarrier. the golden doxorubicin for oncological applictions. *ACS applied materials & interfaces*, *8*(31), 19946-19957.

Development of smart core/shell NPs as a drug platform for their further use in cancer therapy

Dounia Louaguef[1], Eric Gaffet[1], Halima Alem-Marchand[1,2]

[1] Institut Jean Lamour, UMR 7198 CNRS-Université de Lorraine
[2] Institut Universitaire de France (IUF)

Abstract:

Core/shell nanoparticles offer promising applications in nanomedicine due to their multifunctionality. Special attention has been paid to superparamagnetic core/shell iron oxide nanoparticles (SPIONs) for targeted cancer therapy[1]. The design of the nanoparticles developed in this work is based on the surface initiated controlled polymerization of monomers at the surface of iron oxide-based core. These new nanomaterials can take advantages of the physical properties of the core and the macromolecular properties of the responsive shell (a responsive co-polymer was grown from our process). These smart nanomaterials are then capable of carrying an anticancer drug and delivering it at controlled temperature into the physiological environment near the tumor site. The final nanomaterials can then combine hyperthermia and chemotherapy[2]. In this work, different sizes of iron oxide core/shell nanoparticles doped with zinc and manganese ($Zn_{0.4}Fe_{2.6}O_4$ @ $MnFe_2O_4$) were synthesized by thermal decomposition and functionalized by a thermoresponsive copolymer based on (2-(methoxy ethoxy)ethyl methacrylate/ethylene glycol methacrylate (MEO_2MA/OEGMA)). To induce cancer targeting and internalization of the nanoparticles towards the cancer cells, the synthesized nanoparticles were functionalized with folic acid, since these cells overexpress receptors that bind folate α[3]. In this work we will present our recent results about the new nanomaterials that we are developing and their complete characterization.

Keywords: Responsive nanomaterials, Core/shell Nanoparticles, SPIONS, Drug delivery, cancer targeting.

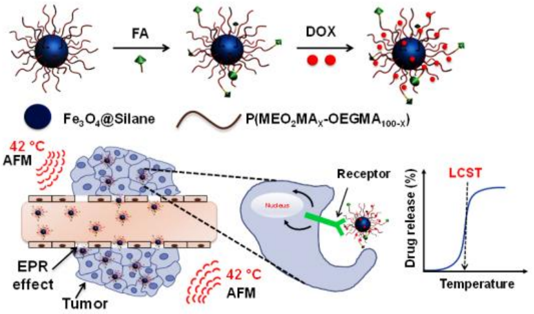


Figure 1: smart core/shell SPIONs for targeted canecr therapy.

References:

1. Cardona JEM, Louaguef D, Gaffet E, Ashammakhi N, Alem H. Review of core/shell nanostructures presenting good hyperthermia properties for cancer therapy. *Mater Chem Front*. 2021;5(17):6429-6443.
2. Ferjaoui Z, Jamal Al Dine E, Kulmukhamedova A, et al. Doxorubicin-Loaded Thermoresponsive Superparamagnetic Nanocarriers for Controlled Drug Delivery and Magnetic Hyperthermia Applications. *ACS Appl Mater Interfaces*. 2019;11(34):30610-30620.
3. Ferjaoui Z, Schneider R, Meftah A, Gaffet E, Alem H. Functional responsive superparamagnetic core/shell nanoparticles and their drug release properties. *RSC Adv*. 2017;7(42):26243-26249.

Development of an effective tumor-targeted contrast agent for Magnetic Resonance Imaging based on Mn/H-Ferritin nanocomplexes

Lucia Salvioni[§],[1]Chiara Tullio[§],[1] Michela Bellini,[1] Anna Degrassi,[2] Luisa Fiandra,[1] Massimiliano D’Arienzo[3], Filippo Testa,[1] Davide Prosperi,[1] Miriam Colombo[1]

[1]NanoBioLab, Department of Biotechnology and Bioscience, University of Milano-Bicocca, Piazza della Scienza 2, 20126 Milano, Italy.
[2]Preclinical Development, Efficacy and Safety, Accelera S.R.L. – NMS Group S.p.A., viale Pasteur 10, 20014 Nerviano (MI), Italy.
[3]Department of Materials Science, University of Milano-Bicocca, Via Roberto Cozzi 55, 20125 Milano, Italy.

Abstract:

Magnetic resonance imaging (MRI) is one of the most sophisticated diagnostic tools that is routinely used in clinical practice. Contrast agents (CAs) are commonly exploited to afford much clearer images of detectable organs and to reduce the risk of misdiagnosis caused by limited MRI sensitivity [1]. Currently, only a few gadolinium-based CAs are approved for clinical use. Concerns about their toxicity remain and their administration is approved only under strict controls [2]. Here we report the synthesis and validation of a novel manganese-based CA, namely Mn@HFn-RT. Manganese is an endogenous paramagnetic metal able to produce a positive contrast like gadolinium, but it is thought to result in less toxicity for the human body [3]. Mn ions were efficiently loaded inside the shell of a recombinant H-Ferritin, which is selectively recognized by the majority of human cancer cells through their transferrin receptor 1 [4]. Mn@HFn-RT was characterized, showing excellent colloidal stability, superior relaxivity, and a good safety profile. In vitro experiments confirmed the ability of Mn@HFn-RT to efficiently and selectively target breast cancer cells. In vivo, Mn@HFn-RT allowed the direct detection of tumors by positive contrast enhancement in a breast cancer murine model, using very low metal dosages and exhibiting rapid clearance after diagnosis. Hence, Mn@HFn-RT is proposed as a promising CA candidate to be developed for MRI.

Keywords: MRI; manganese; H-ferritin; tumor targeting; contrast agent; diagnostic imaging.

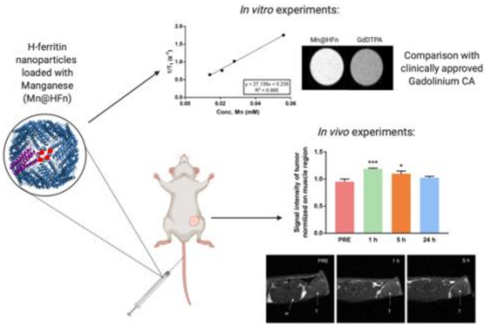


Figure 1: Graphical abstract of the project – H-ferritin nanoparticles loaded with manganese were developed and tested in vitro and in vivo for their contrast power.

References:

1. De León-Rodríguez, L. M.; Martins, A. F.; Pinho, M. C.; Rofsky, N. M.; Sherry, A. D. Basic MR relaxation mechanisms and contrast agent design. J. Magn. Reson. Imaging. 2015, 42, 545–565. http://doi.org/10.1002/jmri.24787
2. https://www.ema.europa.eu/en/news/meeting-highlights-committee-medicinal-products-human-use-chmp-16-19-november-2009.
3. García-Hevia, L.; Bañobre-López, M.; Gallo J. Recent Progress on Manganese-Based Nanostructures as Responsive MRI Contrast Agents. Chemistry. 2019, 25(2):431-441. https://doi.org/10.1002/chem.201802851
4. M. Bellini, M.; B. Riva, B.; V. Tinelli, V., M.A. Rizzuto, M.A; L. Salvioni, L.; M. Colombo, M.; F. Mingozzi, F.; A. Visioli, A.; L. Marongiu, L.; G. Frascotti, G.;. Christodoulou, M.S; Passarella, D.; Prosperi, D.; Fiandra, L.; Engineered Ferritin Nanoparticles for the Bioluminescence Tracking of Nanodrug Delivery in Cancer. Small. 2020, 16 (39). https://doi.org/10.1002/smll.202001450

Nanopore Sensing of Single-Biomolecule: Challenges in Protein Sequencing using Solid-State Nanopores

Adrien Nicolaï, Andreina Urquiola Hernàndez and Patrick Senet

Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne
Franche-Comté, 9 Av. A. Savary, BP 47 870, F-21078 Dijon Cedex, France.

Abstract:

Solid-state nanopores (SSN) made of 2-D materials such as molybdenum disulfide (MoS_2) have emerged as one of the most versatile sensors for single- molecule detection. One of the most promising applications of SSN is DNA and protein sequencing, at a low cost and faster than the current standard methods. The detection principle relies on measuring the relatively small variations of ionic current as charged biomolecules immersed in an electrolyte traverse the nanopore, in response to an external voltage applied across the membrane [1]. The passage of a biomolecule through the pore yields information about its structure and chemical properties, as demonstrated experimentally particularly for DNA molecules. Indeed, protein sequencing using SSN remains highly challenging since the protein ensemble is far more complex than the DNA one. In the present work, we focus on challenges in protein sequencing using solid-state nanopores. Three challenges are highlighted using Molecular Dynamics to simulate protein translocation experiments through MoS_2 nanopores. First, the threading of the protein through the nanopore is discussed [2]. Second, the modification of the nanopore dimensions in order to slow down the passage of the protein through the pore is detailed [2]. Finally, the application of time series analysis tools in order to identify protein sequence motifs from measured raw data is presented and discussed [3].

References:

1. María Daniela Barrios Pérez, Adrien Nicolaï, Patrice Delarue, Vincent Meunier, Marija Drndić, and Patrick Senet. Improved model of ionic transport in 2-D MoS_2 membranes with sub-5 nm pores. *Appl. Phys. Lett.*, 114(2):023107, January 2019.
2. Adrien Nicolaï, Maria Daniela Barrios Pérez, Patrice Delarue, Vincent Meunier, Marija Drndić, and Patrick Senet. Molecular Dynamics Investigation of Polylysine Peptide Translocation through MoS_2 Nanopores. *J. Phys. Chem. B*, 123(10):2342–2353, March 2019.
3. Adrien Nicolaï, Aniket Rath, Patrice Delarue, and Patrick Senet. Nanopore sensing of single-biomolecules: a new procedure to identify protein sequence motifs from molecular dynamics. *Nanoscale*, 12(44):22743–22753, November 2020.

A biophotonics-based biosensor for extracellular vesicles characterization in Alzheimer's disease patients

S. Picciolini[1*], A. Gualerzi [1], F. Rodà[1], M.Bedoni[1]

[1] IRCCS Fondazione Don Carlo Gnocchi, Laboratory of Nanomedicine and Clinical Biophotonics (LABION), Milan, Italy

Abstract:

One of the main hurdle in the rehabilitation and treatment of neurological diseases is the lack of easily accessible and sensitive biomarkers for the prediction of the progression rate and the evaluation of therapy efficacy. Extracellular Vesicles (EVs) represent promising nanosized biomarkers of Alzheimer's disease (AD), being involved in its onset and progression [1]. In the strive for a reliable and sensitive method to analyze EVs, we propose a biophotonics-based biosensor that takes advantage of Surface Plasmon Resonance imaging (SPRi) technique.

We applied our recently optimized SPRi biosensor [2] for the detection and characterization of EVs isolated from the blood of AD patients. The SPRi-array was designed to separate simultaneously EVs released by neurons, astrocytes, microglia and oligodendrocytes, and to evaluate the presence and the relative amount of specific surface molecules related to pathological processes, such as neuroinflammation and formation of β-amyloid plaques.

Our results showed differences in the relative amount of specific cell-derived EV populations, and also in their membrane molecules between healthy subjects and AD patients. The EVs characterization demonstrated the presence of nanovesicles loaded with altered cargoes in AD patients: variations in the activation phenotype of microglia EVs and differences in the lipid moieties on brain-derived EVs were observed.

Our results provide support for using the SPRi-based biosensor for the detection and characterization of circulating EVs to evaluate their potential as peripheral biomarkers for the diagnosis and monitoring of AD patients and the evaluation of the rehabilitation outcomes in a personalized way.

Keywords: Extracellular Vesicles, Surface Plasmon Resonance imaging, Biosensor, Alzheimer's disease

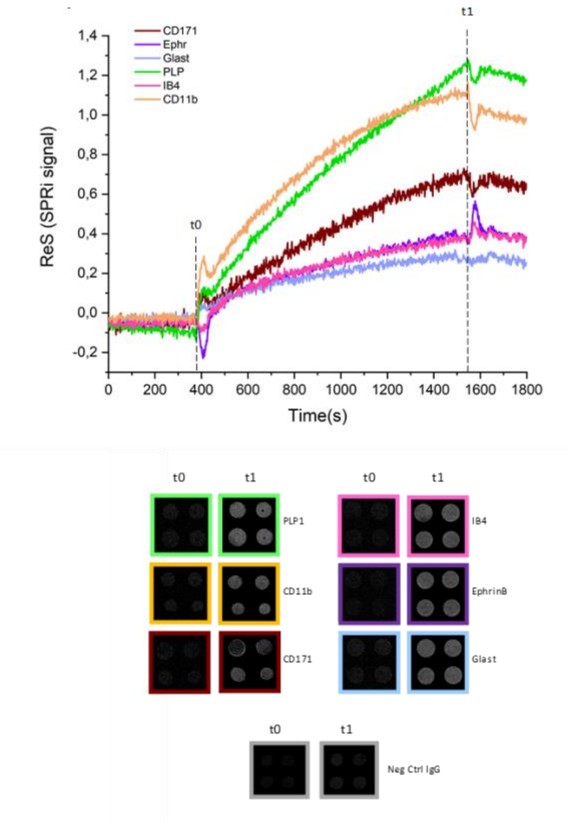


Figure 1: SPRi sensorgram related to EVs injection on an array of 7 ligands (specific for different neural populations of EVs). t0 indicates the time when the injection of the sample starts, and t1 when it ends. Each signal is the substraction between the signal obtained on the specific ligand family and the signal obtained on the Negative ctrl family spotted on the same chip. CCD differential images of each spots on the SPRi chip acquired at t0 and t1.

References:

1. Joshi P, et al. *International Journal of Molecular Sciences*. 2015;16(3):4800-4813.
2. Picciolini S, et al. *Analytical Chemistry*. 2018;90(15):8873-8880.

Biophotonics-based characterization of multifunctionalized liposomes as therapeutic agents for Glioblastoma and Alzheimer's Disease

F. Rodà[1]*, S. Picciolini[1], A. Gualerzi[1], F. Re[2], A. Antoniou[3], S. Giofré[3], P. Seneci[3], M. Bedoni[1]

[1] IRCCS Fondazione Don Carlo Gnocchi, Laboratory of Nanomedicine and Clinical Biophotonics (LABION), Milan, Italy
[2] School of Medicine and Surgery, University of Milano Bicocca, Monza, Italy
[3] Department of Chemistry, University of Milan, Milano, Italy

Abstract:

Neurological diseases represent some of the most dramatic and poorly treated diseases with a considerable social and economic impact. The research for successful treatment is a grand challenge due to the presence of the blood brain barrier (BBB) that limits drugs access to the brain. Nanomedicine has led to the development of nanoparticle-based drug delivery systems and, among them, liposomes are the most studied thanks to their capacity to hold a large payload of drugs and their biocompatibility[1]. In this study, we exploited the biophotonic techniques, Surface Plasmon Resonance Imaging (SPRi) and Raman Spectroscopy (RS) as innovative tools for the validation of engineered liposomes (LPs) for the control of neuroinflammation and associated microglial dysfunctions in Glioblastoma and Alzheimer's Disease. Liposomes, loaded with selected drugs, have been also functionalized with mApoE to cross the BBB[2], and with protease sensitive peptides to guarantee the effective and localized release of the candidate drugs in diseased areas where some specific proteases are overexpressed. SPRi analysis was performed in order to evaluate the binding affinity and kinetics of the LPs to their target receptors, whereas RS was used to verify the quality and the reproducibility of LPs synthesis. Our SPRi results confirmed the presence of mApoE thanks to the specific interaction with the selected receptors. The preliminary test for assessing the binding kinetic between LPs and mApoE targets showed that mApoE-LPs have a higher affinity (low K_D) compared to not functionalized LPs. The PCA-LDA analysis on the Raman dataset allowed to statistically discriminate the spectra collected from the LPs functionalized and not functionalized with mApoE, demonstrating that RS can distinguish each LP-component. In conclusion, our results demonstrated the ability of biophotonics-based tools to evaluate the preservation of the binding affinity of mApoE and to obtain a specific chemical fingerprint for each formulation.

Keywords: liposomes, Surface Plasmon Resonance imaging, Raman Spectroscopy, biophotonics, neurological disease

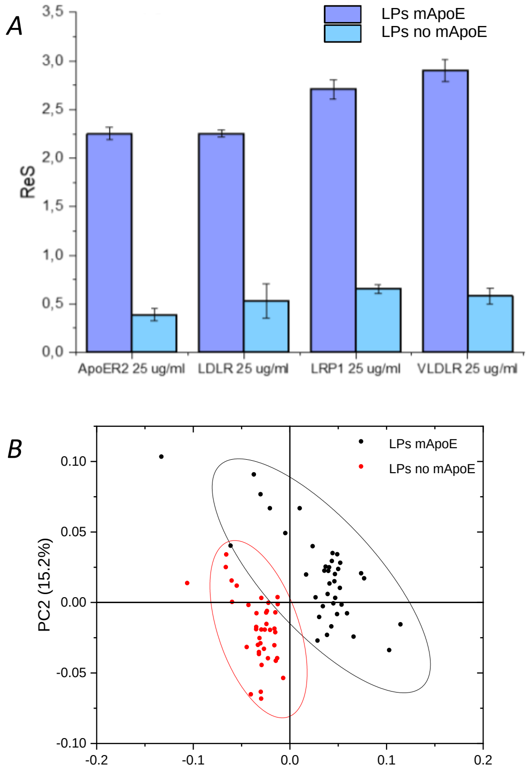


Figure 1: A) Comparison of SPRi signal intensities (ReS) between LPs functionalized and not functionalized with mApoE towards the targets. B) Results of the Principal Component Analysis on the different LP formulations.

Supported by Fondazione regionale per la Ricerca Biomedica (FRRB).

References:

1. Beltran-Gracia et al., *Cancer Nano*, 2019
2. F. Re et al., *Nanomedicine Nanotechnology, Biol. Med.*, 2011

Development of DOTAREM-Gold-Complex: A new multifunctional nanotheranostic agent for Cholangiocarcinoma

Memona Khan, Nadia Djaker, Jolanda Spadavecchia,
CNRS, UMR 7244, CSPBAT, Laboratory of Chemistry, Structures and Properties of Biomaterials
And Therapeutic Agents University Paris 13, Sorbonne Paris Nord, Bobigny, France

Abstract:

Dotarem (DOT) is a macrocyclic contrast agent of type T_1 used in magnetic resonance imaging (MRI) (1). This contrast agent is known as a non-toxic and effective to improve the contrast of MRI images (1). The particularity of DOT is to have gadolinium in the core and DOTA, around it to protect. Thus, gadolinium remains effective while being less toxic to the body.

In this work we propose a new therapeutic strategy, in which we combined contrast agent and drug on the same nanoparticles by chelation methodology (Method IN) (2).

For this purpose, Firstly, we have synthetized bimetallic Au-DOT nanoparticles by complexation and stabilized them with lactose-modified Chitosan, Chitlac (CTL) (3). The choice of polymer was done because of its anti-cancer properties and also because it recognizes the protein Galectin-1 (Gal-1), overly expressed on cancer cells. The next step will be to add the drug, Gemcitabine by two methods IN and ON and evaluate the efficiency on KKU-M213, cholangiocarcinoma cells.

The optimized synthesis was evaluated by physicochemical spectroscopies (UV-VIS, SERS, TEM). On SERS technique we can identify characteristic peaks of the complexation of gold and COO^- of DOT. *In vitro* experiments showed that these nanoparticles alone are not toxic for the cells but when we irradiate it with a laser of 808 nm, we can see a clear cell death. More, relaxivity measures by MRI, has shown effectiveness of contrast with these nanoparticles. This study demonstrated these nanoparticles can be suitable for diagnosis and therapy.

Keywords: Nanothernostic, MRI, bimetallic nanoparticles, Gold, Gadolinium, Dotarem, Phototherapy, biomedical applications.

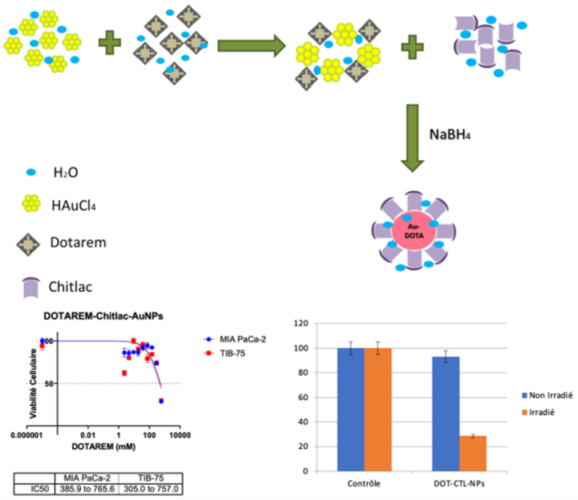


Figure 1: Figure illustrating the synthesis of Au-DOT, stabilized by CTL. The graph represents the IC50 of this synthesis on the cells, Mia-PaCa-2 and TIB-75. A Histogram representing cells death after irradiation by 808 nm laser.

References:

1. Ramalho, J., Semelka, R. C., Ramalho, M., Nunes, R. H., AlObaidy, M., & Castillo, M. (2016). Gadolinium-based contrast agent accumulation and toxicity: an update. *American Journal of Neuroradiology*, *37*(7), 1192-1198.
2. Khan, M., Boumati, S., Arib, C., Diallo, A. T., Djaker, N., Doan, B. T., Spadavecchia, J. (2021). Doxorubicin (DOX) Gadolinium–Gold-Complex: A New Way to Tune Hybrid Nanorods as Theranostic Agent. *International Journal of Nanomedicine*, *16*, 2219.
3. Liu, Q., Sacco, P., Marsich, E., Furlani, F., Arib, C., Djaker, N., ... & Spadavecchia, J. (2018). Lactose-modified chitosan gold (III)-PEGylated complex-bioconjugates: from synthesis to interaction with targeted Galectin-1 protein. *Bioconjugate chemistry*, *29*(10), 3352-3361

Magnetic nanoparticles to stimulate nerve regeneration on a neuroepithelial stem cell model

S. De Vincentiis[1*], M. Baggiani[1], J. Lopane[1], V. Cappello[2], M. Mainardi[3], M. Di Caprio[2], A. Falconieri[1], M. Costa[3], M. Onorati[1], V. Raffa [1]

[1] Department of Biology, University of Pisa, Pisa, Italy
[2] Bio@SNS, Scuola Normale Superiore, Pisa, Italy
[3] Neuroscience Institute, National Research Council (IN-CNR), Pisa, Italy

Abstract:

Spinal cord injury (SCI) is a multifactorial pathology. The permanent disability caused by SCI is related to the failure of axon regeneration and neural circuit reconstruction, due to multiple inhibitory barriers that affect axon growth as well as remyelination (1). Among the different cellular and molecular approaches to treat SCI (2), an innovative method consists in the transplantation of stem cells at the lesion site, in order to reconstruct damaged spinal circuits. However, transplanted cell survival and differentiation in the injured spinal cord is low, possibly because transplanted cells take several weeks, even months, to differentiate *in vivo*. While many groups are investigating the possibility to stimulate this process with chemical factors (2), we are proposing the use of mechanical forces to overcome these problems. Even though recent studies show that mechanical forces are able to stimulate every phase of axonal growth (3), their use to accelerate the differentiation of neural precursor cells in mature neurons have rarely been investigated. Therefore, we focused on the effects of mechanical stimulus on the differentiation and maturation processes of an *in vitro* model of human neuroepithelial stem cells. The technology was already validated by our team for inducing stretch-growth of axons of mice hippocampal neurons (4). The protocol is based on the labeling of cells with magnetic nanoparticles, and the use of a magnetic field gradient to generate a traction force that stretches the neurites. Althought this force was extremely low (i.e. less than 10 pN) our results indicate both an increase in neurite elongation (Figure 1) and an acceleration of neuronal maturation. Althought further experiments are needed, this approach seems promising to boost differentiation efficiency in stem cell transplantation for the treatment of SCI.

Keywords: Nanoparticles, magnetic field, spinal cord injury, human neural stem cells, maturation, regeneration.

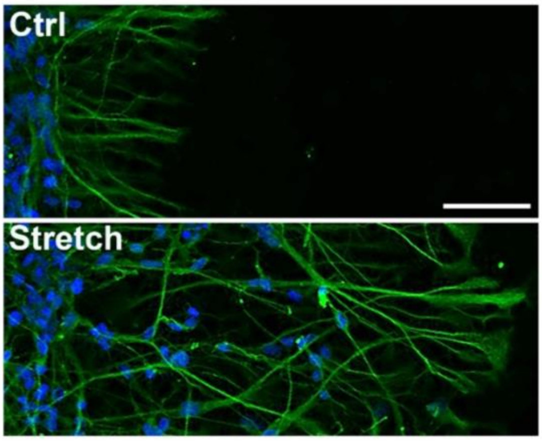


Figure 1: Representative images of control (Ctrl) and stretched condition (Stretch) at day *in vitro* 10, after 2 days of stretching. Scale bar 100 nm.

References:

1. Sofroniew, MV., (2018) Dissecting spinal cord regeneration, *Nature*, 557, 343-350.
2. Griffin, JM., Bradke, F. (2020) Therapeutic repair for spinal cord injury: combinatory approaches to address a multifaceted problem, *EMBO Mol Med.*, 12, 3, 3.
3. De Vincentiis, S., Falconieri, A., Scribano, V., Ghignoli, S., Raffa, V. (2020), Manipulation of axonal outgrowth via exogenous low forces, *Int. J. Mol Sci.*, 21(21):8009.
4. De Vincentiis, S., Falconieri, A., Mainardi, M., Cappello, V., Scribano, V., Bizzarri, R., Storti, B., Dente, L., Costa, M., Raffa, V., Extremely low forces induce extreme axon growth (2020), J Neurosci., 40(26):4997-5007.

Toxicity of carbon nanomaterials - towards reliable viability assessment via new approach in flow cytometry

T. Malina [1,2,*], K. Poláková [1,2,*], C. Hirsch [3], L. Svoboda [4, 5], R. Zbořil [1, 4]
[1] Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute, Palacký University, Křížkovského 511/8, 779 00 Olomouc, Czech Republic
[2] Department of Physical Chemistry, Faculty of Science, Palacký University Olomouc, Křížkovského 511/8, 779 00 Olomouc, Czech Republic
[3] Laboratory for Particles-Biology Interactions, Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland
[4] Nanotechnology Centre, Centre of Energy and Environmental Technologies, VŠB−Technical University of Ostrava, 17. Listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic
[5] IT4Innovations, VŠB – Technical University of Ostrava, 17. listopadu 15/2172, Ostrava 708 00, Czech Republic

Abstract:

The scope of application of carbon nanomaterials (CNMs) in biomedical, environmental and industry fields has been recently substantially increasing. Since *in vitro* toxicity testing is the first essential step for any commercial usage, it is crucial to have a reliable method to analyze potential harmful effects of CNMs. Even though researchers already reported the interference of CNMs with common toxicity assays, there is still, unfortunately, large number of studies that neglect this fact. In this study, we investigated interference of four bio-promising CNMs (graphene acid (GA), cyanographene (GCN), graphitic carbon nitride (g-C3N4) and carbon dots (CDs)) in commonly used LIVE/DEAD assay. When a standard procedure was applied, CNMs caused various types of interference. While positively charged g-C3N4 and CDs induced false results through creation of free agglomerates and intrinsic fluorescence properties, negatively charged GA and GCN led to false signals due to complex quenching effect of fluorescent dye of a LIVE/DEAD kit. Thus, we developed a new approach using specific gating strategy based on additional controls that successfully overcame all of CNM interferences and lead to reliable results in LIVE/DEAD assay. We suggest that the newly developed procedure should be a mandatory tool for all in vitro flow cytometry assays of any class of CNMs.

Keywords: Carbon nanomaterials, Flow cytometry, Cell viability, Cytotoxicity, Interference

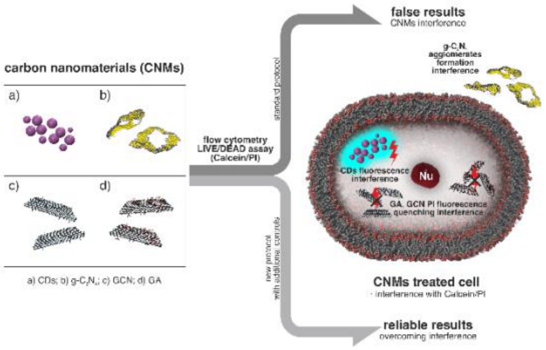


Figure 1: Ilustration scheme of four types of emerging carbon nanomaterials (left) and various types of their interference with commercial dyes used in flow cytometry (right). Only by using our new approach with additional controls, it is possible to achieve reliable results of cell viability endpoint.

References:

1. Malina, T.; Poláková, K.; Hirsch, C.; Svoboda, L.; Zbořil, R. (2021) Toxicity of Carbon Nanomaterials—Towards Reliable Viability Assessment via New Approach in Flow Cytometry. *Int. J. Mol. Sci.*, 22, 7750..

European Graphene Forum - EGF 2021
Onsite Session I

Advances in Organic 2D Crystals

Xinliang Feng
Center for Advancing Electronics Dresden & Faculty of Chemistry and Food Chemistry,
Technische Universitaet Dresden; Max Planck Institute of Microstructure Physics, Germany
xinliang.feng@tu-dresden.de

Abstract:

Over the last decade, the discovery of graphene has triggered a new paradigm of two-dimensional (2D) crystal materials. They are characterized by a periodic network structure and topographical thickness at the atomic/molecular level, enabling the investigation of fundamental exotic physical and chemical properties down to a single-layer nanosheet. Thereby, robust technologies and industrial applications, ranging from electronics and optoelectronics to energy storage, energy conversion, membranes, sensors, and biomedicine, have been inspired by the discovery and exploration of such new materials.

In contrast to the tremendous efforts dedicated to the exploration of graphene and inorganic 2D crystals such as metal dichalcogenides, boron nitride, black phosphorus, metal oxides, and nitrides, there has been much less development in organic 2D crystalline materials, including the bottom-up organic/polymer synthesis of graphene nanoribbons, 2D metal-organic frameworks, 2D polymers/supramolecular polymers, as well as the supramolecular approach to 2D organic nanostructures. One of the central chemical challenges is to realize a controlled polymerization in two distinct dimensions under thermodynamic/kinetic control in solution and at the surface/interface. In this talk, we will present our recent efforts in bottom-up synthetic approaches towards novel organic 2D crystals with structural control at the atomic/molecular level and beyond. We will introduce a surfactant-monolayer assisted interfacial synthesis (SMAIS) method that is highly efficient to promote supramolecular assembly of precursor monomers on the water surface and subsequent 2D polymerization in a controlled manner. 2D conjugated polymers and coordination polymers belong to such materials classes. The unique structures with possible tailoring of conjugated building blocks and conjugation lengths, tunable pore sizes and thicknesses, as well as impressive electronic structures, make them highly promising for a range of applications in electronics and spintronics. Other application potential of organic 2D crystals, such as in membranes, will also be discussed.

References:

Chem. Commun. **2009**, 6919; Adv. Mater. **2015**, 27, 403; Angew. Chem. Int. Ed. **2015**, 54, 12058; J. Am. Chem. Soc. **2015**, 137, 14525; Nature Comm. **2015**, 6, 8817; Nature Comm. **2016**, 7, 13461; Polym. Chem. **2016**, 7, 4176; Angew. Chem. Int. Ed. **2017**, 56, 3920; Chem. Rev. **2018**, 118, 6189; Nature Comm. **2018**, 9, 1140; Nature Comm. **2018**, 9, 2637; Nature Mater. **2018**, 17, 1027; Angew. Chem. Int. Ed. **2018**, 130, 13942; Nature Comm. **2019**, 10, 3260; Nature Chem. **2019**, 11, 994; Nature Comm. **2019**, 10, 4225; Nature Comm. **2020**, 11, 1409; J. Am. Chem. Soc. **2020**, 142, 12903; Angew. Chem. Int. Ed. **2020**, 59, 8218; Anew. Chem. Int. Ed. **2020**, 59, 6028; Anew. Chem. Int. Ed. **2020**, 59, 23620; Science Adv. **2020**, 6, eabb5976; Nature Mater. **2021**, 20, 122; Chem. Soc. Rev. **2021**, 50, 2764; Anew. Chem. Int. Ed. **2021**, 60, 13859.

Graphene Oxide and Derivatives, Properties and Applications

B. Gjoka,[1*] R. Wendelbo,[1]
[1] Abalonyx As, Forskningsveien 1, 0373, Oslo, Norway

Abstract:

Graphene oxide (GO) is most often- prepared in labs using Hummers method[1] , but this method is unsafe to scale up beyond 10 grams. GO is a convenient intermediate for large scale production of graphene-like materials such as reduced graphene oxide (rGO).[2,3] In our Company, we have developed a safe, scalable and inexpensive method to provide GO of similar quality to Hummers method GO in Kg-scale.

The acidity of both GO and rGO can be reduced by washing with water or even neutralized by treatment with ammonium hydroxide or other bases. The sheets can be small or large, all these variations giving rise to a large family of related compounds with multiple properties, suitable for different applications, including such diverse technologies as loudspeaker membranes, water treatment, polymer composites, protective coatings, sports equipment, energy storage and medical applications. We see several applications now being piloted around the globe and a few reaching industrial application. In general, thermal reduction of graphene oxide has shown better results in terms of reduction degree (C/O ratio) compared to chemical methods. The material obtained in Abalonyx is implemented in different formulation such as paste and sheet, in order to enhance conductivity performances in electronic applications.

For each method applied, the scalability of the process was explored and optimized together with the QC and standardisation of the modified material.

Additionally, to expand graphene oxide-like materials and show its versatility in terms of chemical modification, covalent functionalization with amine groups were performed.[4] For example, amine-based GO has found use in many fields such as composites, catalysis, electronics and water treatment. Such modifications were implemented not only to enhance and modulate the properties of graphene oxide, but also to provide reproducible and scalable functionalized graphene oxide materials which has been Abalonyx focus for more than 7 years. Morover, these modifications will provide better dispersion in different organic solvents (Figure 1). Different techniques were employed to have reproducible processes for both reduction and functionalization methodologies of graphene oxide, in view of large-scale production.

Keywords: Graphene oxide, Reduced graphene oxide, Functionalization, Industrial Applications, GO Quality Control, Characterization 2D Materials.

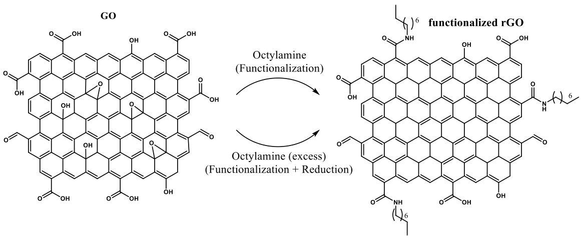


Figure 1: General scheme for GO Reduction and functionalization.

References:

1. Hummers, W.S., Offeman, R.E. (1958) Preparation of Graphitic Oxide, *J. Am. Chem. Soc.*, 80, 1339
2. Dreyer, D., S Park, S., C W. Bielawski, C. W., and Ruoff, R. (2010), The Chemistry of Graphene Oxide, *Chem. Soc. Rev.*, 39, 228-240.
3. Chen, D., Feng, H., Li, J. (2012), Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications, *Chem. Review*, 112, 6027-6053.
4. Tian, Sh., Liu, Zh., Shen, L., Pu, J., Liu, W., Sun. X. Li, Zh. (2018), Performance evaluation of mercapto functional hybrid silica sol–gel coating and its synergistic effect with f-GNs for corrosion protection of copper surface *RSC. Adv.*, 8, 7438- 7449.

Liquid-Phase Exfoliation of Graphene: Comparison of Laser-Induced Graphene and Graphite as Precursors

B. Kulyk [1,*], A. F. Carvalho [1], D. Santos [1], B. F. R. Silva [1], A. J. S. Fernandes [1], B. R. Figueiredo [2], R. P. Silva [2], V. E. Abrantes [2], A. Bernardes [2], F. M. Costa [1]
[1] i3N, Department of Physics, University of Aveiro, Aveiro, Portugal
[2] Graphenest, Sever do Vouga, Portugal

Abstract:
The application of graphene at an industrial scale dependes on the ability to produce it in large quantities while preserving its structural quality and unique properties. In this context, the field of high-throughput top-down production methods such as liquid-phase exfoliation of graphite has seen a lot of activity, both in academia and in industry. In particular, sonication exfoliation has yielded stable dispersions of suspended few-layer graphene flakes, stimulating the use of this material in a wide-range of composites and coatings. In parallel, the synthesis of graphene foams by laser irradiation has been emerging over the last several years as a facile method to obtain graphene, compatible with the concept of continuous production. The resulting material, known as laser induced graphene (LIG), can be derived from a wide assortment of substrates, from commercial polymers such as polyimide to materials such as paper, cork and wood. In this work, we perform sonication dispersion in organic solvents of LIG obtained from different substrates (Figure 1). The resulting suspensions are characterized in terms of particle size, crystalline quality, morphology, and stability. Accordingly, the results will be compared with a commercial process based on liquid-phase exfoliation of natural graphite. This study sheds light on the viability of high-throuput production of few-layer graphene flakes obtained from LIG, informing future potential manufacturing approaches and technological applications.

Keywords: graphene, laser-induced graphene, polyimide, paper, cork, liquid-phase exfoliation.

Acknowledgements:
This work was developed within the scope of the projects: “GNESIS” Project 33566 (POCI-01-0247-FEDER-033566), financed by FEDER through POCI, and i3N Project (UIDB/50025/2020 & UIDP/50025/2020) financed by national funds through the FCT.
Bohdan Kulyk thanks FCT for the PhD grant SFRH/BD/141525/2018.

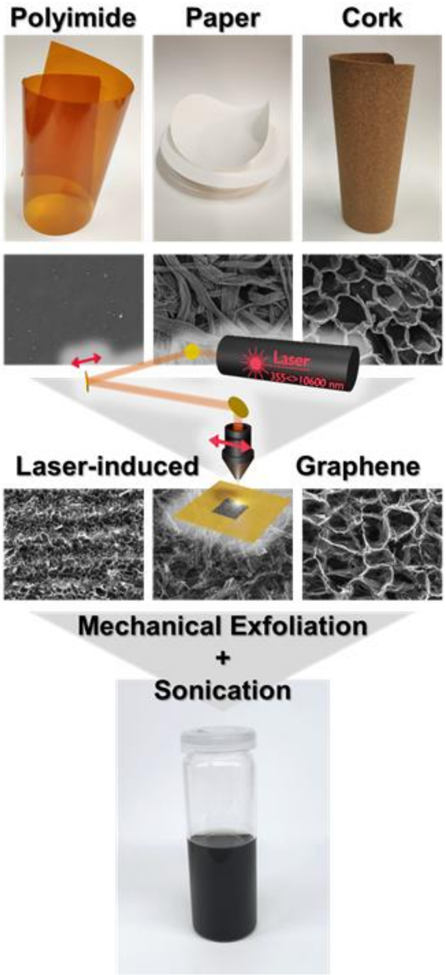


Figure 1: Schematic representation of the production of graphene suspensions using LIG from different substrates as the bulk graphene source.

References:

1. Kulyk, B. *et al.* (2021), *ACS Appl. Mater. Interfaces*, 13, 8, 10210-10221, doi: 10.1021/acsami.0c20270
2. Carvalho, A. F. *et al.* (2020), *Adv. Mater. Technol.*, 5, 2000630, doi: 10.1002/admt.202000630
3. Kulyk, B. *et al.* (2021), *Crit. Rev. Solid State Mater.*, doi: 10.1080/10408436.2021.1886046

Steam reforming towards freestanding gas-phase few-layer graphene

P. Fortugno*, H. Wiggers, C.Schulz

IVG, Insitute for Combustion and Gas Dynamics – Reactive Fluids, and CENIDE Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47057 Duisburg, Germany

Abstract:

Since its discovery in 2004, graphene triggered remarkable interest in many different research fields due to its unique electrical and mechanical properties. Possible applications include electrical components such as sensors, transparent electrodes, and transistors. In addition, graphene is a promising component of various composite materials, e.g. for electrochemically active materials and for polymers [1]. For these composites, reliable high-throughput synthesis methods are needed to satisfy the demand in case of commercialisation. Typical methods for producing freestanding graphene are usually thermal or wet-chemical exfoliation of graphene oxide. These methods are usually troubled by their non-continuous approach and the requirement for costly and aggressive chemicals that in addition can lead to contamination of the product and the presence of undesired phases. In addition, a chemical reduction process is often required to produce materials with good electrical conductivity.

A simple and scalable alternative to these processes is the direct gas-phase synthesis of freestanding graphene based on an atmospheric pressure microwave plasma process, where a hydrocarbon precursor is decomposed in a plasma. We present results from our work on the use of different precursor and showcase a simple strategy on how to affect the formed carbon phase and tune it towards the formation of few-layer graphene (FLG) through the addition of water vapor. By precisely adjusting the process parameters, FLG can be formed directly from the gas phase due to nucleation downstream of the plasma zone. The chemical purity of the produced materials is exceptional and outperforms reduced graphene oxides in battery applications [2] and activated carbon in catalysis [3]. Raman spectroscopy is used to judge the product quality (Figure 1). With the help of spectroscopic methods, we propose how water interacts with the carbon phase to synthesize high-purity graphene.

Keywords: Plasma, large scale synthesis, freestanding graphene, gas-phase, steam reforming

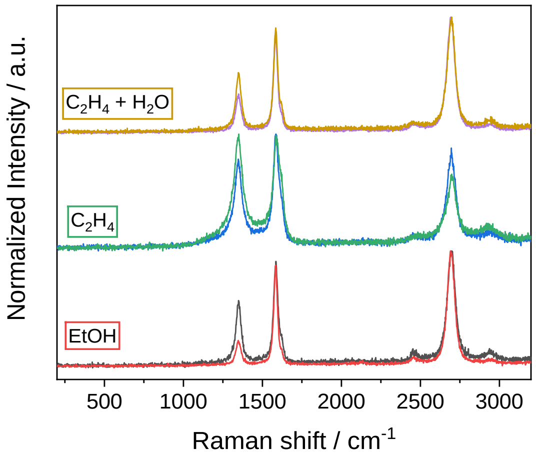


Figure 1: Raman spectra of carbon samples prepared with different gas-phase compositions.

References:

1. Ferrari, A.C., et al., *Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems.* Nanoscale, 2015. 7(11): p. 4598-4810.
2. Münzer, A., et al., *All gas-phase synthesis of graphene: Characterization and its utilization for silicon-based lithium-ion batteries.* Electrochimica Acta, 2018. 272: p. 52-59.
3. Bertin, E., et al., *Durability study of platinum nanoparticles supported on gas-phase synthesized graphene in oxygen reduction reaction conditions.* Applied Surface Science, 2019. 467-468: p. 1181-1186.

Solution Processed Graphene-Nanographene van der Waals Heterostructures for Photodetectors with Efficient and Ultralong Charge Separation

Zhaoyang Liu,[1] Shuai Fu,[2] Akimitsu Narita,[2] Artur Ciesielski,[1] Mischa Bonn,[2] Klaus Müllen,[2] Hai I. Wang,[2] Paolo Samorì[1,]*
[1] University of Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, 67000 Strasbourg, France
[2] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Abstract:
Graphene is highly attractive in photonics and optoelectronics applications thanks to its extraordinary physical properties. However, the modest light absorption of monolayer graphene and the short (~picosecond) lifetime of the photo-generated hot carriers result in relatively low internal quantum efficiency, thus limiting the availability of pristine graphene in photodetection.[1]
Sensitization of graphene with inorganic semiconducting nanostructures has been demonstrated as a powerful strategy to boost its optoelectronic performance.[2] However, the limited tunability of optical properties and toxicity of metal cations in the inorganic sensitizers prohibits their widespread applications, and the in-depth understanding of the essential interfacial charge transfer process within such hybrid systems remained elusive. Here, we design and develop high-quality nanographene (NG) dispersions with a large-scale production using high-shear mixing exfoliation (Figure 1). The physisorption of these NG molecules onto graphene gives rise to the formation of graphene-NG van der Waals heterostructures (VDWHs), characterized by strong interlayer coupling through π-π interactions. As a proof of concept, photodetectors fabricated based on such VDWHs show ultrahigh responsivity up to 4.5 x 10^7 A/W and a specific detectivity reaching 4.6×10^{13} Jones, being competitive with the highest values obtained for graphene-based photodetectors. The outstanding device characteristics is attributed to the efficient transfer of photogenerated holes from NGs to graphene and the long-lived charge separation at graphene-NG interfaces (beyond 1 ns), as elucidated by ultrafast terahertz (THz) spectroscopy. These results demonstrate the great potential of such graphene-NG VDWHs as prototypical building blocks for high-performance optoelectronics.

Keywords: graphene, nanographene, van der Waals heterostructures, photodetectors, ultralong charge separation.

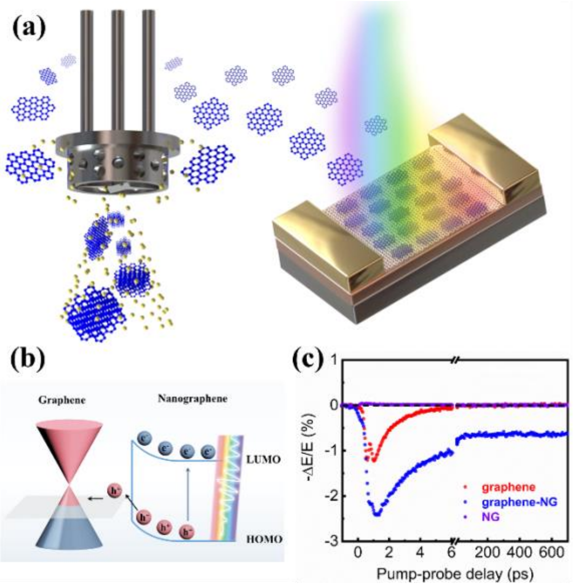


Figure 1: General concept of solution processed graphene-NG van der Waals heterostructures: a) Schematic illustration of the shear mixing exfoliation process to achieve monodispersed nanographene molecules, and the fabricated photodetector with a FET configuration comprising graphene-NG VDWHs. b) Working mechanism of the photoresponsive graphene-NG VDWHs: under illumination, photogenerated holes transfer from NG to graphene, while the photogenerated electrons remain in the NG layer. c) THz photoconductivity dynamics suggesting the ultralong charge separation (beyond 1 ns) at the graphene-NG interfaces.

References:

1. F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, M. Polini, *Nat. Nanotechnol.* **2014**, *9*, 780.
2. a) G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. de Arquer, F. Gatti, F. H. L. Koppens, *Nat. Nanotechnol.* **2012**, *7*, 363; b) K. Roy, M.

Padmanabhan, S. Goswami, T. P. Sai, G. Ramalingam, S. Raghavan, A. Ghosh, *Nat. Nanotechnol.* **2013**, *8*, 826.

Visible-frequency plasmons in nanocorrugated graphene

P. Vancsó [1*], G. Dobrik [1], P. Nemes-Incze [1], B. Majerus [2], P. Süle [1], G. Piszter [1], M. Menyhárd, B. Kalas [1], P. Petrik [1], L.Henrard [2], L. Tapasztó [1]
[1] Institute of Technical Physics and Materials Science, Centre for Energy Research, Budapest, Hungary
[2] Department of Physics, Namur Institute of Structured Matter, University of Namur, Namur, Belgium

Abstract:

An effective way to engineer the electronic and optical properties of graphene is via quantum confinement of its charge carriers. Such quantum confinement is usually realized through physical edges and is able to open sizeable band gaps or tune the plasmon resonance frequencies from the native terahertz regime. However, edges come with major drawbacks due to the strong inter-valley scattering of the charge carriers, which reduce the mobility and significantly damp palsmon resonances. Therefore, in order to avoid inter-valley scattering alternative confiment techniques, downscaling the structure size into the sub-10 nm range, are necessary.

In this talk, we will present that nanocorrugations are able to confine effectively the charge carriers in graphene resulting in an improved conductivity and several plasmon like optical excitations at visible frequencies based on our ab-initio calculations (Figure 1). We have experimentally realized such graphene sheets with unprecedentedly strong nanocorrugations (< 5 nm lateral size, > 0.4 aspect ratio) by using thermal annealing process. The predicted visible graphene plasmons can mediate significantly stronger light-matter interactions (Raman enhancement) compared to flat graphene, allowing the detection of specific molecules. We have demonstrated this Raman enhancement by measuring Raman signal of ZnPc and CuPc molecules from femtomolar solutions or even ambient air. Our nanocurrugated graphene substrates offer a versatile material platform for graphene plasmonics at visible frequencies.

Keywords: corrugated graphene, Raman spectroscopy, ab initio electronic and optical calculations, plasmons

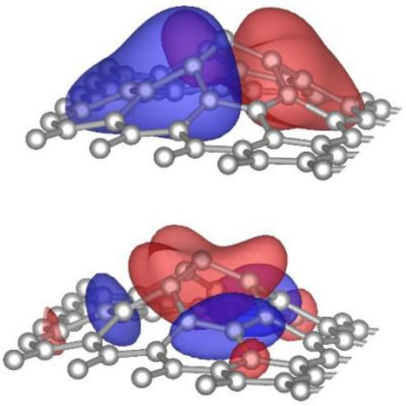


Figure 1: Charge distributions of optical excitations corresponding to loss peak near 1.9 eV and 2.9 eV from our calculated EELS spectrum of a model graphene nanocorrugation.

References:

1. Dobrik, G., Nemes-Incze, P., Majerus, B., Süle, P., Vancsó, P., Piszter, G., Menyhárd, M., Kalas, B., Petrik, P., Henrard, L., Tapasztó L. (2021) Large-area nanoengineering of graphene corrugations for visible-frequency graphene plasmons, *Nat. Nanotechnol., accepted.*

2D layered metal phosphorous trichalcogenides for electrochemical energy conversion reactions

Rui Gusmão
[1] Department of Inorganic Chemistry, Faculty of Chemical Technology, University of Chemistry and Technology Prague, Prague, Czech Republic

Abstract:
Owing to their unique physical and chemical properties, layered two-dimensional (2D) materials have been established as the most significant topic in materials science for the current decade. This includes layers comprising mono-element (graphene, phosphorene), di-element (TMD, MXene), and even multi-element. The 2D layered materials are currently one of the most explored materials for developing efficient and stable electrocatalysts for energy conversion applications. A distinctive class of 2D layered materials is the metal phosphorous trichalcogenides (MPX_3, X=S, Se), having unusual intercalation. [1] Some of the 2D MPX_3, have been reported to be useful catalysts for water splitting,[1,2] although the results have been less promising for the sluggish oxygen evolution reaction (OER) due to insufficient activity or compromised stability.

We report on the water splitting performance of a series of MPX_3 (M^{2+} = Mn, Fe, Co, Zn, Cd; X = S, Se). For the series of MPX_3, $CoPS_3$ yields the best results with an overpotential within the range of values usually obtained for IrO_2 or RuO_2 catalysts.[3] The liquid-phase exfoliation of $CoPS_3$ improves the OER activity due to the abundant active edges of the downsized sheets, accompanied by the presence of surface oxides. The influence of the OER medium and the underlying substrate electrode is studied, with the exfoliated $CoPS_3$ reaching the lowest overpotential also able to sustain high current densities, with excellent stability after multiple cycles or long-term operation.

The photoelectrochemical (PEC) responsivity of MPX_3 was also tested in the OER region, with excitation wavelengths from 385 to 700 nm, is reported. [4] The experimentally determined optical bandgaps of the MPX_3 materials range from 1.5 eV for $FePSe_3$ to 3.7 eV for $ZnPS_3$. At +1.23 V vs. RHE, the PEC activity in the OER region of $MnPSe_3$ exhibits superior performance, while the exfoliation of $CoPS_3$ improves its PEC activity up to double in contrast with its bulk counterpart. The influence of the substrate and applied potential is also optimized.

Keywords: 2D, layered materials, synthesis, liquid-phase exfoliation, top-down methods, chatacterization, (photo)electrochemistry, water splitting, hydrogen evolution, oxygen evolution, oxygen reduction

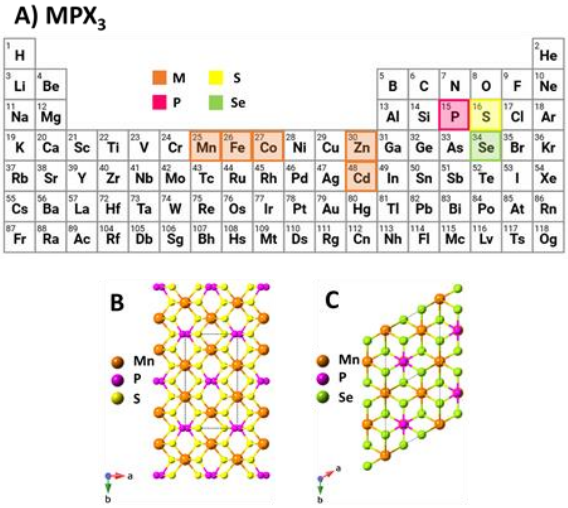


Figure 1: (A) Periodic table in which the filled blocks represent the elements selected for the synthesis of MPX3 materials. Top (c-axis) view of the crystal structures of (B) MnPS3 and (C) MPSe3. Color scheme: Mn – orange, P – pink, S – yellow, Se – green.

References:

1. R. Gusmão *et al.* Adv. Funct. Mater. 29 (2019) 1805975.
2. R. Gusmão *et al.* Angew. Chemie - Int. Ed. 58 (2019) 9326–9337.
3. F.M. Oliveira *et al.* Adv. Mater. Interfaces (2021) 2100294.
4. F.M. Oliveira *et al.* ACS Appl. Mater. Interfaces 13 (2021) 23638–23646.

Biodegradability and safety of carbon and bi-dimensional nanomaterials

A. Bianco
CNRS, Immunology, Immunopathology and Therapeutic Chemistry, UPR 3572, University of Strasbourg, ISIS, 67000 Strasbourg, France

Abstract:
Graphene-based and bi-dimensional (2D) nanomaterials are showing very promising results in the biomedical field. They are explored for many different biomedical applications, including cancer treatment, due to their unique physicochemical characteristics. In this seminar, I will describe the characteristics of biodegradability and illustrate how an appropriate chemical modification of these materials renders them more biocompatible and can accelerate their biodegradability (1). I will focus on our recent results aiming to design a smart multifunctional graphene platform able to both selectively deliver a drug into cells in a targeted manner and displaying an enhanced propensity for enzymatic degradation. Moreover, I will address the safety aspects of graphene-based and 2D materials on immune system, focusing on human primary lymphocytes, monocytes and macrophages (2).

Keywords: Graphene, carbon materials, degradation-by-design, biomedical applications, cytotoxicity, immune system, peroxidases.

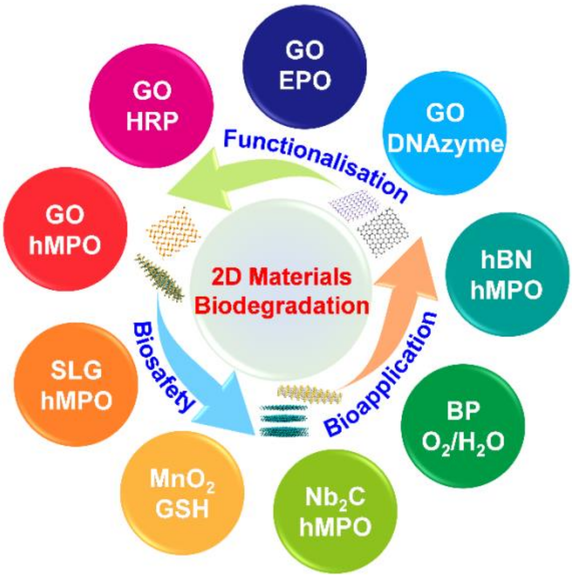


Figure 1: Figure illustrating the different types of graphene and 2D materials and the enzymes capable to degrade them [GO, graphene oxide; SLG, single layer graphene, BP, black phosphorus; hBN, hexagonal boron nitride, HRP, horseradish peroxidase; hMPO, human myeloperoxidase; EPO, eosinophil peroxidase; GSH glutathione].

References:

1. Ma, B., Martìn, C., Kurapati, R., Bianco, A. (2020), Degradation-by-design: how chemical functionalisation enhances the biodegradability and safety of 2D materials, *Chem. Soc. Rev.*, 49, 6224-6247
2. Lin H., Song, Z., Bianco, A. (2021), How macrophages respond to two-dimensional materials: a critical overview focusing on toxicity, *J. Env. Sci. Health, Part B*, 56, 333-356.

Low Pt loading Hierarchical Oxygen Reduction Electrocatalysts with a Graphene *“Core”* and a Carbon Nitride *“Shell”*

Vito Di Noto [1,2,*], Enrico Negro [1,3], Angeloclaudio Nale [1], Keti Vezzù [1,2], Gioele Pagot [1,3]
[1] Dept. of Industrial Engineering, University of Padova, via Marzolo 9, 35131, Italy
[2] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Italy
[3] Centro Studi *“Giorgio Levi Cases”*, Via Marzolo 9, 35131, Italy
*E-mail of the Corresponding Author: vito.dinoto@unipd.it

Abstract:
As of today a major restructuring of the energy system at the global level is taking place, with the ultimate goal to minimize the dependence from fossil fuels and curtail the emissions of greenhouse gases. A shift of paradigm is necessary towards the widespread implementation of innovative energy conversion and storage technologies. In this regard, a pivotal role is expected for electrochemical energy conversion and storage (EECS) systems owing to their independence from geographical constrains, facile scalability and outstanding efficiency. In this regard, proton exchange membrane fuel cells (PEMFCs) are very attractive owing to their outstanding efficiency, compatibility with the environment and ease of implementation in diverse applications such as auxiliary power units, light-duty vehicles and trucks.

This contribution overviews the development of an innovative family of electrocatalysts (ECs) to improve the kinetics of the oxygen reduction reaction (ORR). This latter process is a crucial bottleneck in PEMFC operation and requires ECs comprising a high loading of platinum, a critical raw material prone to trigger supply bottlenecks. This is a major drawback inhibiting the large-scale rollout of PEMFCs. On these bases, it is clear that the development of high-performance and durable ECs that comprise a low loading of platinum (giving so rise to *“Low-Pt ECs”*) is a major goal of PEMFC research.

The ECs here described include a low loading of Pt and are characterized by active sites located on the surface of sub-nanometric clusters (SNCs) where Pt is alloyed with a first-row transition metal (*e.g.*, Ni, Cu). The latter operates as a *“co-catalyst”* and raises the intrinsic performance of each active site much above the Pt baseline. The support of the ECs comprises a hierarchical graphene-based (H-GR) *“core”* covered by a carbon nitride (CN) *“shell”*. H-GR consists of highly defective graphene nanoplatelets and carbon black NPs to facilitate mass and charge transport. The CN *“shell”* is decorated with C- and N-based *“coordination nests”* that stabilize the SNCs and boost the durability of the ECs. Herein it is elucidated the interplay between the preparation parameters of the ECs, the physicochemical properties, the electrochemical behaviour and the performance in a single PEMFC tested under operating conditions.

Keywords: Proton-exchange membrane fuel cells, oxygen reduction reaction, low loading of platinum, cyclic voltammetry with the thin-film rotating ring-disk electrode method, membrane-electrode assembly.

Ackowledgements: The research leading to the results reported in this work has received funding from: (a) the European Union’s Horizon 2020 research and innovation programme under grant agreement 881603; (b) the project *“Advanced Low-Platinum hierarchical Electrocatalysts for low-T fuel cells”* funded by EIT Raw Materials; and (c) the project *“Hierarchical electrocatalysts with a low platinum loading for low-temperature fuel cells - HELPER”* funded by the University of Padova.

References:

1. Second Report on the State of the Energy Union, COM (2017) 53, European Commission, Brussels.
2. B. Dunn, H. Kamath, J.M. Tarascon (2011), *Science*, 334, 928-935.
3. V. Di Noto, E. Negro, K. Vezzù, F. Bertasi, G. Nawn (2015), *Electrochem. Soc. Interface*, 24, 59-64.
4. V. Di Noto, E. Negro, A. Bach Delpeuch, F. Bertasi, G. Pagot, K. Vezzù (2017), *Patent application PCT/EP2017/084801*.

Symmetry of Electron Bands in Graphene: (Nearly) Free Electron Versus Tight-Binding

E. Kogan [1*], V. M. Silkin[2,3]
[1] Department of Physics, Bar-Ilan University, Ramat-Gan, Israel
[2] Donostia International Physics Center (DIPC), Donostia, Spain
[3] Departmento de Polímeros y Materiales Avanzados: Física, Química y Tecnología Facultad de Ciencias Químicas Universidad del País Vasco (UPV/EHU), San Sebastián-Donostia, Basque Country, Spain

Abstract:

We compare the classification of the electron bands in graphene, obtained by group theory algebra in the framework of a tight-binding model (TBM),with that calculated in a density-functional-theory (DFT) framework. Identification in the DFT band structure of all eight energy bands (four valence and four conduction bands) corresponding to the TBM-derived energy bands is performed and the corresponding analysis is presented. The four occupied (three σ-like and one π-like) and three unoccupied (two σ-like and one π-like) bands given by the DFT closely correspond to those predicted by the TBM, both by their symmetry and their dispersion law.

However, the two lowest lying at the _-point unoccupied bands (one of them of a σ-like type and the other of a π-like one), are not of the TBM type. According to both their symmetry and the electron density these bands are plane waves orthogonal to the TBM valence bands; dispersion of these states can be determined unambiguously up to the Brillouin zone borders. On the other hand, the fourth unoccupied band given by the TBM can be identified among those given by the DFT band calculations; it is situated rather high with respect to energy. The interaction of this band with the free-electron states is so strong that it exists only in part of the *k* space.The symmetry labeling of all electron bands in graphene obtained by combining numerical band calculations and analytical analysis based on group theory is

presented. The latter is performed both in the framework of the (nearly) free electron model, or in the framework of the tight-binding model. The predictions about relative positions of the bands which can be made on the basis of each of the models just using the group theory (and additional simple qualitative arguments, if necessary) are complimentary.

Keywords: band calculations, graphene, group theory, image states, tight-binding approximation

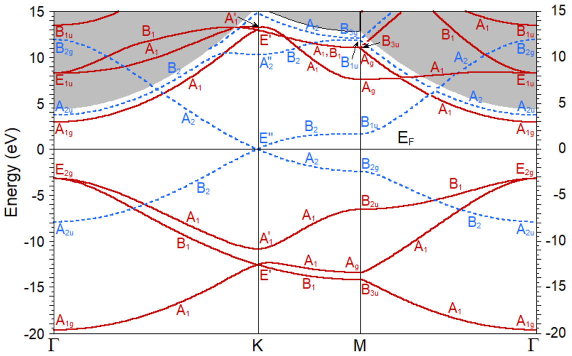


Figure 1: Calculated graphene band structure with labeling of states at the symmetry points and symmetry directions of the BZ. The σ-like bands are plotted with red solid lines and the π-like bands—with blue dashed lines. The gray area corresponds to the vacuum continuum states. The black horizontal line shows the Fermi energy position.

References:

1. Kogan, E., Nazarov, V. U., Silkin, V. M., Kaveh, M. (2014), Energy bands in graphene: Comparison between the tight-binding model and ab initio calculations, Phys. Rev. B 89, 165430 1-7.
2. Kogan, E., Silkin V. M. (2017), Electronic structure of graphene: (nearly) free electrons bands vs. tight-binding bands, Phys. Stat. Sol. B, 254, 1700035 1-8.
3. Kogan, E., Silkin V. M. (2021), Symmetry of electron bands in graphene: (nearly) free electron vs. tight-binding,, Phys. Stat. Sol. B, 258, 2000504 1-9.

Screening properties of graphene and its effect on electronic states

V. M. Silkin[1,2,3*], E. Kogan[4], G. Gumbs[5]
[1] Donostia International Physics Center (DIPC), San Sebastián, Spain
[2] Departmento de Polímeros y Materiales Avanzados: Física, Química y Tecnología Facultad de Ciencias Químicas Universidad del País Vasco (UPV/EHU), San Sebastián, Spain
[3] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain
[4] Department of Physics, Bar-Ilan University, Ramat-Gan, Israel
[5] Department of Physics and Astronomy, Hunter College of the City Univeristy of New York, USA

Abstract:

In difference to surfaces of solids, in a free-standing graphene sheet a double Rydberg series of even and odd image-potential states with energies between the Fermi level and the vacuum level can be realized [1]. Image-potential states in graphene placed on various substrates have been investigated by two-photon photoemission and scanning tunnelling spectroscopy [2-10]. In addition, several works proposed different descriptions for the electron potential in free-standing and supported graphene [2,3,11-13]. However in all these studies a key ingredient – an image plane position z_{im} – was not addressed explicitly in construction of an electric potential designed to describe the image-potential states. Thus, in Refs. [1,11], it was assumed that z_{im} is located at the carbon atom plane, which seems reasonable for a such almost two-dimensional electronic system. On the other hand, the value of 0.99 Å for z_{im} was obtained employing the fitting procedure in the model potential construction [14].

In order to determine z_{im}, in this work we performed a systemic study of the electronic structure of free-standing graphene exposed to a uniform perpendicular external electric field considering several geometries. The calculations were carried out within the framework of the first-principles density functional theory employing the norm-conserving ionic pseudopotential approach. Our calculations provide reliable information regarding the z_{im} position for graphene and allow us to construct new hybrid atomic potentials for description of its electronic structure. Using these potentials, we obtain new data for the binding energies of the image-potential states in graphene.

Keywords: graphene, image-plane position, image-potential states
Approximation

References:

1. Silkin, V. M., Zhao, J. , F. Guinea, Chulkov, E. V., Echenique, P. M., Petek, H. (2009) *Phys. Rev. B* 80, 121408(R) .
2. Bose, S., et al. (2010), *New J. Phys.* 12, 023028.
3. Borca, B., et al. (2010), *Phys. Rev. Lett.* 105, 036804.
4. Armbrust, N., Güdde, J., Jakob, P., Höfer, U. (2012), *Phys. Rev. Lett.* 108, 056801.
5. Craes, F., Runte, S., Klinkhammer, J., Kralj, M., Michely, T., Busse, C. (2013), *Phys. Rev. Lett.* 111, 056804.
6. Nobis, D., Potenz, M., Niesner, D., Fauster, Th. (2013), *Phys. Rev. B* 88, 195435.
7. Takahashi, K., Imamura, M., Yamamoto, I., Azuma, J., Kamada, M. (2014), Phys. Rev. B 89, 155303.
8. Niesner, D., Fauster, Th. (2014), *J. Phys. : Condens. Matter* 26, 393001.
9. Lin, Y., Li, Y. Z., Sadowski, J. T., Jin, W. C., Dadap, J. I., Hybertsen, M. S., Osgood, R. M. (2018), *Phys. Rev. B* 97, 165413.
10. Fan, L., Lee, S. K., Chen, P. Y., Li, W. (2018), *J. Phys. Chem. Lett.* 9, 1485.
11. De Andres, P. L., Echenique, P. M., Niesner, D., Fauster, Th., Rivacova, A. (2014), *New J. Phys*. 16, 023012.
12. Ambrust, N., Güdde, J., Höfer, U. (2015), *New J. Phys.* 17, 103043.
13. Hamada, I., Hamamoto, Y., Morikawa, Y. (2017), *J. Chem. Phys.* 147, 044708.
14. Armbrust, N., Güdde, J., Höfer, U. (2015), *New J. Phys.* 17, 103043.

Electron Diffraction and Photoemission from Few-Layer Graphene

Eugene Krasovskii [1,2,3,*]
[1] University of the Basque Country, Donostia / San Sebastián, Spain
[2] Donostia International Physics Center (DIPC), Donostia / San Sebastián, Spain
[3] IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

Abstract:

Apart from its unique electronic structure at the Fermi level, graphene manifests fascinating electron scattering features in the ultra-violet range, highly relevant for the electron diffraction and photoelectron spectroscopy. The measurements of electron transmission and photoemission from one to few-layer graphene involves interesting scattering processes that do not occur in other materials.

Here, an overview of scattering phenomena in graphene and related materials will be presented, as well as their theoretical description within an *ab initio* quantum mechanical theory [1]. The electronic structure of a graphene monolayer above the vacuum level is discussed in the context of discrete states immersed in the three-dimensional continuum. Scattering resonances are shown to exist, which originate from the coupling of the in-plane and perpendicular electron motions, as elucidated by the analysis of an exactly solvable model [1]. The resonances are theoretically shown and experimentally confirmed to lead to a total reflection of the incident electron below and total transmission above the resonance energy, see Figure 1. A strong en-hancement of photoemission intensity is theoretically predicted to occur around the scattering resonances [2]. Scattering by few-layer films is discussed for hexagonal boron nitride. The presence of electron transmission slits due to the interlayer scattering in few-layer graphene and h-BN opens a way to study subtle quantum properties of the interlayer states [3]. A combination of low energy electron reflection and transmission electron microscopy allows to detect rapid energy variations of the transverse mean free path and questions the validity of the “universal” mean free path curve [4].

Furthermore, graphene is a promising material for studying temporal characteristics of scattering, in particular within the concept of Wigner delay: How long does it take for the electron to traverse a thin layer? A qualitative difference between resonant and nonresonant scattering will be discussed.

Keywords: graphene, low energy electron diffraction, photoelectron spectroscopy, scattering resonances, electronic structure, *ab initio* methods, augmented plane waves.

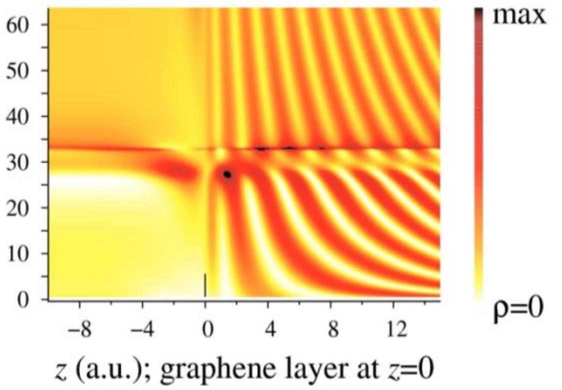


Figure 1 Energy-depth distribution $\rho(z,E)$ of the probability density of the scattering states for a graphene monolayer (electron is incident from the right) [1]. Scattering resonance at 28 eV above the Fermi level is seen as a sharp enhancement of the density.

References:

1. Nazarov, V.U., Krasovskii, E.E., and Silkin, V.M. (2013) Scattering resonances in two-dimensional crystals with application to graphene *Phys. Rev. B*, 87, 041405.
2. Krasovskii, E.E. (2021) Ab Initio Theory of Photoemission from Graphene *Nanomaterials*, 11, 1212.
3. Jobst, J., *et al.* (2016) Quantifying electronic band interactions in van der Waals materials using angle-resolved reflected-electron spectroscopy *Nat. Commun.*, 7, 13621.
4. Geelen, D., *et al.* (2019) Nonuniversal Transverse Electron Mean Free Path through Few-layer Graphene *Phys. Rev. Lett.*, 123, 086802.

Graphene Quantum Dots Bolometers for Studies of Single Molecule Magnets

L. St Marie[1], L. Havlicek[2], J. Hruby[2], A. Alqahtani[1], D. Henry[1], A. Sojka[2], J. Navarro[2], R. Myers-Ward[3], D. Gaskill[4], A. El Fatimy[5], A. Liu[1], I. Nemec[2, 6], P. Neugebauer[2], P. Barbara[1]

[1] Department of Physics, Georgetown University, Washington, DC, USA
[2] Central European Institute of Technology, Brno University, Brno, Czech Republic
[3] US Naval Research Laboratory（NRL）, Washington DC, USA
[4]Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, MD, USA
[5]Present address: Ecole Centrale Casablanca, Casablanca, Morocco
[6]Department of Inorganic Chemistry, Palacký University, Olomouc, Czech Republic

Abstract:

Single molecule magnets (SMMs) are clusters of magnetic ions or single ions embedded in a ligand shell and they can be modeled as single-spin quantum systems. Their spectra have an energy barrier to magnetization reversal yielding magnetic bistabilty at low temperature and widely spaced spin states, making them very attractive for high-density data storage, molecular spintronics and quantum computing. SMMs are mostly studied in bulk samples, i.e. single crystals or powder pellets. However, since most applications require SMMs deposited on surfaces, it is important to understand whether the interaction between the ligand shells and the surfaces may substantially alter the SMM properties.

Here we use epitaxial graphene on SiC patterned into quantum dots to probe the properties of SMMs. Since the detectors are designed with the graphene surface fully exposed, SMMs can be deposited directly on the graphene. The graphene quantum dots serve as highly sensitive photodetectors for *in-situ* electron paramagnetic resonance (EPR) spectroscopy of the SMMs, to measure whether the spectra of SMMs on the graphene surface are modified with respect to the spectra of SMMs in bulk samples.[1-3]

The interaction between the SMMs and the graphene also affects the transport properties of the quantum dot. We study this effect and the EPR spectra for $Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4$, as well as for a version of these SMMs with modified O_2CCHCl_2 carboxylate ligands.[4]

Keywords: Graphene, quantum dots, bolometers, single-molecule magnets, electron paramagnetic resonance.

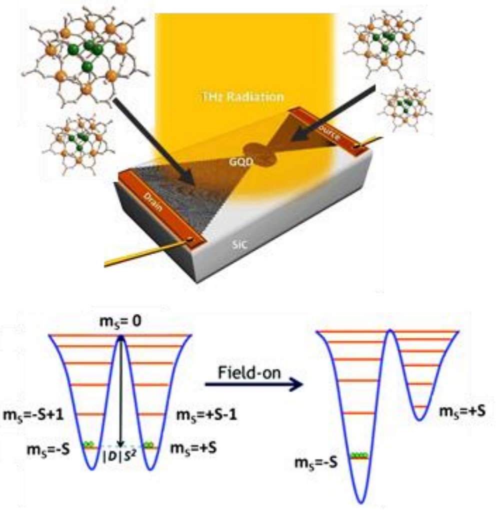


Figure 1: Top: Schematic of a graphene quantum dot bolometer decorated with Mn_{12} SMMs. Bottom: Mn_{12} energy spectrum in zero magnetic field and with a magnetic field applied.

References:

1. El Fatimy, A.; Myers-Ward, R. L.; Boyd, A. K.; Daniels, K. M.; Gaskill, D. K.; Barbara, P. *Nature Nanotechnology* **2016,** 11, (4), 335-+.
2. El Fatimy, A.; Nath, A.; Kong, B. D.; Boyd, A. K.; Myers-Ward, R. L.; Daniels, K. M.; Jadidi, M. M.; Murphy, T. E.; Gaskill, D. K.; Barbara, P. *Nanophotonics* **2018,** 7, (4), 735-740.
3. St Marie, L.; El Fatimy, A.; Hruby, J.; Nemec, I.; Hunt, J.; Myers-Ward, R.; Gaskill, D. K.; Kruskopf, M.; Yang, Y. F.; Elmquist, R.; Marx, R.; van Slageren, J.; Neugebauer, P.; Barbara, P. *Journal of Physics-Materials* **2020,** 3, (1).
4. Zhu, X. C.; Hale, A.; Christou, G.; Hebard, A. F. *Journal of Applied Physics* **2020,** 127, (6).

Electrochemical Remediation of Chlorinated Ethenes Contamination Using N-functionalized Graphene Electrode

Hui Ma[a*], Hans Christian Bruun Hansen[a]
[a] Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

Abstract:

The application of electrochemical reductive dehalogenation for remediation of soils and waters contaminated with chlorinated solvents is hindered by the high cost of cathode materials and low Faradaic efficiency. Chlorinated ethenes (CEs), especially the less chlorinated ones, rank among the most frequent contaminants in groundwater. We report that nitrogen (N)-functionalized graphene is an effective cathode material for CEs reduction.

A robust post-N-doping approach is used to produce N-graphene. N-functional groups were induced without causing structural defects. The I_G/I_D ratio from the Raman spectrum decreased due to the defects coalesce, meanwhile, the longitudinal dimension La of the graphene stack was enlarged. The electron transfer resistance R_{ct} of the N-graphene decreased compared with the commercial graphene due to its active sites and higher electrical conductivity. Both reactivity and selectivity of the electrode for different CEs reduction were enhanced. The pyridinic N is identified as the critical active site improving the onset potential for dechlorination.

Approximately 90% of contaminants including vinyl chloride (VC), dichloroethylenes (DCE), trichloroethylene (TCE), and tetrachloroethylene (PCE) at environmental relevant concentrations (10-80 μM) were reduced within 5 h, with Faradaic efficiency ranging from 30 to 60%. The reduction pathway for VC was hydrogenolysis, with ethene and ethane as main products, while dechlorination of PCE, DCE, and TCE followed β-elimination with acetylene as the main product. The electrochemical reduction of contaminants generally followed two mechanisms: direct reduction by the electrode or indirect reduction by atomic H* generated by the electrode. In our study, all dechlorination was mainly due to the direct reduction on the active sites of the N-graphene electrode. To determine the optimal operating parameters for electrolysis remediation, we tested the influence of applied potential, pH, contaminants concentration, and supporting electrolyte concentration. The electrode with good stability only showed less than 5% of reactivity decrease after recycled for more than 5 times.

This study presents the fundamental aspects of the N-functionalization of graphene and opens avenues for the development of graphene as an electrochemical catalyst for remediation of waters contaminated with halogenated compounds.

Keywords: electrochemical dehalogenation, graphene N-functionalization, groundwater contamination, chlorinated ethylenes, metal-free catalyst

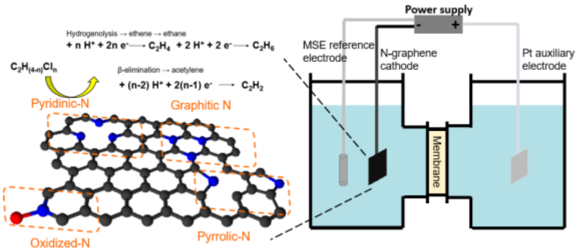


Figure 1: Illustration of mechanisms and experimental setup for CEs reduction by N-graphene cathode. Experiments conditions: CEs concentration ranged from 10 to 80 μM; applied potential -0.387 to -0.787 V vs RHE, 0.01 M Na_2SO_4 with 1*1 cm^2 N-graphene cathode, Pt auxiliary anode and Mercury/Mercurous Sulfate (Sat'd K_2SO_4) reference electrode.

References:

1. Ai, J., Ma, H., Tobler, D.J., Mangayayam, M.C., Lu, C., van den Berg, F.W.J., Yin, W., Hansen, H.C., Bone Char Mediated Dechlorination of Trichloroethylene by Green Rust, (2020), *Environ. Sci. Technol*, 54, 3643-3652.
2. Schiefler, A.A., Tobler, D.J., Overheu, N.D., Tuxen, N. (2018) Extent of natural attenuation of chlorinated ethenes at a contaminated site in Denmark, *Energy Procedia*, 146, 188-193.

Anaerobic Bioreduction of Dye Moleules by Ceramic-Supported Graphene Oxide Membranes

M. S. A. Amin[*], F. Stüber, J. Giralt, A. Fabregat, J. Font
Departament d’Enginyeria Química, Universitat Rovira i Virgili, Tarragona, Spain

Abstract:

Textile wastewater can be treated separately by physical, chemical, and biological processes or in integrated methods. Many chemicals are applied in chemical processes, and the volume of sludge produced in these methods is enormous. For this reason, additional treatments are needed before the discharge of sludges or byproducts into the environment. Physical treatment techniques face similar challenges like chemical treatments due to the problem arisen by slurry, filter cake, operating cost, etc. Biological treatments or activated sludge processes are desirable, as they requires an insignificant amount of chemicals or without any at all. However, the high space requirement to install biological treatment facilities becomes a barrier. In most cases, the responsible agents would not like to invest much more to build large-scale biological plants to treat wastewater. Besides this, most individual treatment procedures are typically non-sustainable and incapable of achieving entire wastewater treatment performance. As a result, a combination of approaches may provide a suitable solution for preventing water contamination. The membrane bioreactor, which may be combined with anaerobic sludge, could be one of the best solutions. An efficient membrane precursor to optimize the decolorization rate must be chosen to accomplish this goal and be compatible to perform under anaerobic conditions. In these circumstances, graphene oxide would be a good precursor because of its superior conductivity and chemical resistance. To our best knowledge, no work has been done yet to combine the graphene oxide membrane in an anaerobic decolorization process in a compact reactor. This research presents a novel integrated technology based on applying ceramic-supported graphene oxide membrane (CSGoM) to degrade dye molecule (Methylene Blue, MB) through anaerobic bio-reduction.

Keywords: Anaerobic decolorization, Carbon Based Membrane, Wastewater treatment

As shown in Figure 1, the synthesized membranes allow the retention of all the biomass that carry out the biodegradation. Furthermore, the carbon layer facilitates the transport of electrons and provides support for the growth of the bioactive film.

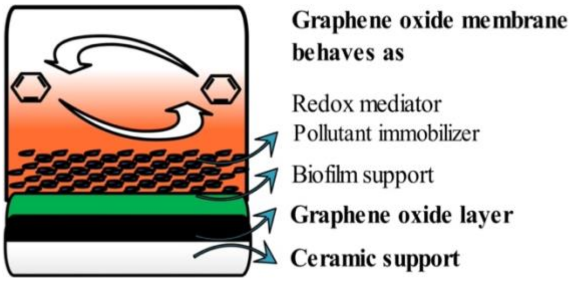


Figure 1: Illustration of the triple role of graphene oxide membrane during the anaerobic biodecolorization of methylene blue dye.

Several experiments with and without micro-organisms or CSGoM reactors were investigated to study the bioreduction of model synthetic methylene blue (MB) dye solution. A maxi-mum dye decolorization, around 98%, was observed at the bioreactors operated with micro-organism and graphene oxide membrane. Thus, the concept of a compact single unit reactor is successfully proven to produce highly treated effluents without the need for subsequent purification steps.

References:

1. Amin, M. S. A., Stüber, F., Giralt, J., Fortuny, A., Fabregat, A., Font, J. (2021) Comparative Anaerobic Decolorization of Azo Dyes by Carbon-Based Membrane Bioreactor. *Water*, 13(8), 1060.
2. Giménez-Pérez, A., Bikkarolla, S. K., Benson, J., Bengoa, C., Stüber, F., Fortuny, A., Papakonstantinou, P. (2016) Synthesis of N-doped and non-doped partially oxidised graphene membranes supported over ceramic materials. *Journal of Materials Science*, 51(18), 8346-8360.

Performance Evaluation of Nitrogen-doped Graphene / Carbon Black Supported Pt_3Co Nanoparticles as PEM Fuel Cell Cathode Electrocatalyst

D. K. Perivoliotis [1,*], X. Jia [1], T. Wågberg [1]
[1] Department of Physics, Umeå University, Umeå 90187, Sweden

Abstract:

In view of the growing demand for energy along with the global climate crisis, polymer electrolyte membrane fuel cells (PEMFCs) have emerged as the most promising and environmentally friendly power sources for application in automobiles and portable electronics. The commercialization of such systems requires the development of new highly efficient and durable cathode electrocatalysts to accelerate the kinetically sluggish oxygen reduction reaction (ORR). In this regard, much effort has been devoted during the past decade aiming at either the development of catalytic nanoparticles with complex nanostructures (i.e., alloyed, core-shell) or the exploration of novel supports. Among the different supporting materials, graphene due to its large surface area, excellent electrical conductivity, and good chemical stability has been widely used as a platform for the construction of ORR electrocatalysts.[1] For most graphene-based electrocatalysts, their performances have been only evaluated in the half-cell test, showing a great potential for further use in PEMFCs; however, they cannot be accurate as they do not represent their activities and durability under real operating conditions. Needless to say, the harsh acidic environment of the most PEMFCs may result in a rapid degradation of the graphene supported nanocatalysts while at the same time other critical parameters like the water permeability of the catalytic layer cannot be assessed.[2] Therefore, there is a compelling need to be conducted more research on the performance of graphene-based electrocatalysts under practical conditions before their application in commercial PEMFC devices. Herein, we enable mixtures of nitrogen-doped graphene (NG) and Vulcan carbon (XC-72R) at different ratios (5:95, 10:90 and 20:80) as platform to realize platinum-cobalt (Pt_3Co) alloyed nanoparticles though a simple and scalable method which involves the reduction of a dry metalorganic precursor blend within a modified commercial household microwave oven[3] followed by a post-annealing treatment. The resulting Pt_3Co/XC-NG catalysts (~10 nm) demonstrated an improved PEMFC performance at 60^o C operating temperature compared to that of Pt_3Co/NG and Pt_3Co/XC references. Actually, the addition of NG to the Vulcan not only allowed us to exploit the exceptional properties of NG but also acted as spacer by yielding a 2D/3D nanoarchitecture with increased porosity and hence significantly facilitates the efficient water management within the membrane electrode assembly (MEA). On the other hand, the surprisingly poor performance of Pt_3Co/NG was ascribed to the low water permeability of the catalytic layer as a result of the stacking of NG nanosheets. The optimum NG to XC ratio was found to be 10:90 with a maximum power density of 390 mW cm^{-2} at an anode and cathode Pt loading of 0.2 mg cm^{-2}. Overall, these results clearly suggest the incorporation of graphene nanosheets into the currently used Vulcan carbon support toward the development of high performance ORR electrocatalyst under practical PEMFC conditions and pave the way for the commercialization of the fuel cell technology.

References:

1. Perivoliotis, D.K., Tagmatarchis, N. (2017) Recent advancements in metal-based hybrid electrocatalysts supported on graphene and related 2D materials for the oxygen reduction reaction, *Carbon*, 118, 493-510.
2. Su, H., Hu, Y.H. (2021) Recent advances in graphene-based materials for fuel cell applications, *Energy Sci Eng.*, 9, 958– 983.
3. Sandström, R., Ekspong, J., Gracia-Espino, E., Wågberg, T. (2019) Oxidatively induced exposure of active surface area during microwave assisted formation of Pt_3Co nanoparticles for oxygen reduction reaction, *RSC Adv.*, 9, 17979-17987

European Graphene Forum - EGF 2021 Virtual Session

Graphene Origami Enabled Negative Poisson’s Ratio in Metal Nanocomposites

J. Yang [1,*]

[1] School of Engineering, RMIT University, PO Box 71, Bundoora, VIC 3083, Australia

Abstract:
Mechanical metamaterials have emerged as a new class of functional materials with unusual material properties. An important example of mechanical metamaterials is auxetic material that exhibits tunable negative Poisson’s ratio. Such materials are attracting considerable interests due to their promising applications. Although enormous studies have been performed to present negative Poisson’s ratio properties in various materials, research work on the auxetic behavior of graphene reinforced metal nanocomposites is still very limited. The present work develops a graphene origami structure to tune the Poisson’s ratio from positive to negative of graphene reinforced copper matrix nanocomposites. Extensive molecular dynamics simulations are conducted to study the tuning mechanism of negative Poisson’s ratio of graphene/Cu composites. The adaptive intermolecular reactive bond order (AIREBO) potential, embedded atom method (EAM) potential, and Lennard-Jones (LJ) potential are employed to simulate the C-C covalent interaction of graphene, the interactions between Cu atoms, and the van der Waal (vdW) interactions between graphene and Cu matrix, respectively. Various graphene origami structures, including Miura pattern, Waterbomb pattern, and Yoshimura pattern, are formed with the assistance of surface hydrogen functionalization in predesigned areas of the graphene sheet. The shape of the graphene origami can be tuned and controlled by changing the content and width of H adatoms in the creases. Afterwards, the designed graphene origami is embedded into a Cu matrix to achieve the tunability of negative Poisson’s ratio. Our results demonstrate that a higher content of graphene origami in composites can lead to a larger negative Poisson’s ratio. In addition, the ambient conditions have considerable effects on the auxetic behaviors of graphene/Cu metamaterials. A greater negative Poisson’s ratio of composites can be achieved in higher temperature and pressure environments. It is also found that bigger folds in graphene origami can help the metal metamaterial to achieve more efficient auxetic properties.

Keywords: metamaterial, negative Poisson’s ratio, graphene origami, metal matrix nanocomposites.

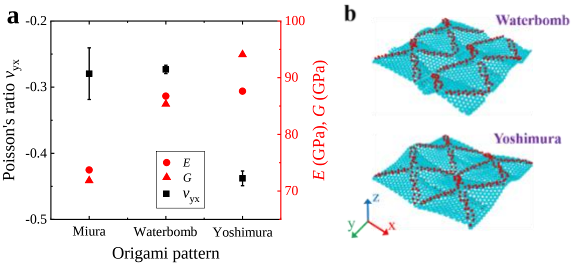


Figure 1: (a) Effect of graphene origami patern on the Poisson’s ratio, Young’s modulus, and shear modulus of graphene origami reinforced copper nanocomposite; (b) different graphene origami patterns.

Acknowledgments

The work was fully supported by the Australian Research Council grant under the Discovery Project scheme (DP210103656). The authors are very grateful for the financial supports.

References:

1. Yu, X., Zhou, J., Liang, H., Jiang, Z., Wu, L. (2018), Mechanical metamaterials associated with stiffness, rigidity and compressibility: A brief review. *Progress Mater. Sci.*, 94, 114-173.
2. Grima, J.N,, Mizzi, L., Azzopardi, K.M., Gatt, R. (2016), Auxetic perforated mechanical metamaterials with randomly oriented cuts. *Adv. Mater.*, 28, 385-389.
3. Wen, Y., Gao, E., Hu, Z., Xu, T., Lu, H., Xu, Z., et al. (2019), Chemically modified graphene films with tunable negative Poisson's ratios. *Nature Communications*. 10, 2446.
4. Zhao, S., Zhang, Y., Yang, J., Kitipornchai S. (2021), Significantly improved interfacial shear strength in graphene/copper nanocomposite via wrinkles and functionalization: A molecular dynamics study. *Carbon*. 174, 335-344.

Mass Production Technology of CVD Graphene Materials for Setting the Cornerstone of Graphene Industry

Zhongfan Liu

Beijing Graphene Institute (BGI)
Center for Nanochemistry (CNC), Peking University, Beijing 100871, China

Abstract:

Mass production of high-quality graphene is the cornerstone of graphene industry. We have been focusing our efforts on chemical vapor deposition (CVD) growth of graphene films over 13 years, starting from lab-scale samples to pilot-scale products and further to commercial products. Fast progress has also been made on the CVD equipments and production lines for meeting the versatile demands of graphene size, quality and production capacity. Our star products include, A3-size graphene films with a single crystalline domain size of ca. 500 micrometers and a production capacity of 10,000 m^2/year, 4-inch and 6-inch single crystal graphene wafers with a capacity of 10,000 wafer/year, 10cm x 30cm superclean graphene films with a capacity of 30,000 pieces/year. Peeling off CVD graphene from growth metal substrate to target substrate is technically very challenging especially for large size graphene films. We have designed our batch-process systems fitting for different graphene products. A team with over 100 members has been created in Beijing Graphene Institute (BGI), covering R& D, equipment manufacturing, production line and marketing, targeting to provide the best quality CVD graphene products and production lines to the world.

Ensuring Robust International Graphene Standards for Industry

Andrew J. Pollard

Abstract:
Although the growing graphene industry worldwide is continuing to deliver new real-world products, without an understanding of the properties of the materials available in the supply chain these new applications cannot be efficiently developed and improved. Thus, there is a need for reliable, accurate and precise measurements for material testing, which are standardised across the industry and therefore allow end-users to be able to compare commercially-available materials from around the world.

The current state of international measurement standards covering the material properties of the graphene family will be detailed, including the ISO/IEC standard “TS 21356-1 Structural characterization of graphene: Graphene from powders and dispersions”. Based on the NPL Good Practice Guide [1] that was developed in collaboration with the University of Manchester, this standard details the techniques and decision making process of characterising the percentage of ‘graphene’ or ‘few-layer graphene’, as defined by ISO [2], in materials sold globally. Importantly, the sample preparation, measurement protocols and data analysis are all described, to enable more reproducible comparisons. The development of the understanding of one of the techniques included in the standard, the Brunauer-Emmett-Teller (BET) method will also be reported.

A key part of developing international measurement standards is the validation of protocols through international interlaboratory comparisons. As an example, the initial results of a VAMAS interlaboratory study, TWA 41 Project 1, on Raman spectroscopy of chemical vapour deposition (CVD) grown graphene will be reported. This project will directly support the development of the ISO/IEC standard “PWI 21356-2 - Structural Characterisation of CVD-grown Graphene”. This interlaboratory study gathered data from 17 participants across academia, industry (including instrument manufacturers) and National laboratories, revealing key metrology issues that must be considered.

References

1. J. Pollard, et al., Characterisation of the structural properties of graphene, NPL Good Practice Guide 145 (2017)
2. ISO, Nanotechnologies -- Vocabulary -- Part 13: Graphene and related two-dimensional (2D) materials, 2017

Quantum Field Theory in Graphene: a Numerical Approach

A. Rodin [1,2]
[1] Yale-NUS College, Singapore
[2] Centre for Advanced 2D Materials, National University of Singapore, Singapore

Abstract:

Graphene's electronic properties are dominated by the p_z orbitals, oriented perpendicularly to the monolayer plane. This orientation produces a modest overlap between the neighboring orbitals, making it possible to construct a tight-binding model with the nearest-neighbor hopping, which captures the essential low-energy physics of the material. In the continuum limit, the Hamiltonian reduces to the famous Dirac form, used extensively to describe transport and excitations in graphene.

Although the Dirac equation is excellent in describing large-scale graphene features, it is less appropriate for studying effects that span a few lattice constants. A standard tool for exploring features on this length scale is the density functional theory (DFT). However, there is an intermediate regime where DFT becomes too computationally costly, while the Dirac equation is not entirely applicable. In this regime, one can employ the tight-binding Hamiltonian without taking the continuum approximation. Unfortunately, without the simplified Dirac form, many integrals become intractable analytically, forcing one to resort to numerical calculations, which can be quite slow.

To facilitate the theoretical study of graphene defects with atomic resolution, we develop an extendable package for Julia language that allows one to efficiently calculate the space-resolved spectral function in the presence of defects. This package can handle an arbitrary arrangement of defects without a decrease in performance, in contrast to DFT and tight-binding calculations where increasing defect separation requires a larger unit cell, resulting in an increased computational cost. At this point, the package can handle graphene coupling to local impurity states (to model adsorbates) and local potential modification (to model local gating). The prototypical form of this package has been used to study the sublattice-resolved interaction between impurities and the role in buckling in hydrogen adsorption in graphene.

Keywords: quantum field theory, numerical, graphene, Julia, spectral function, defects.

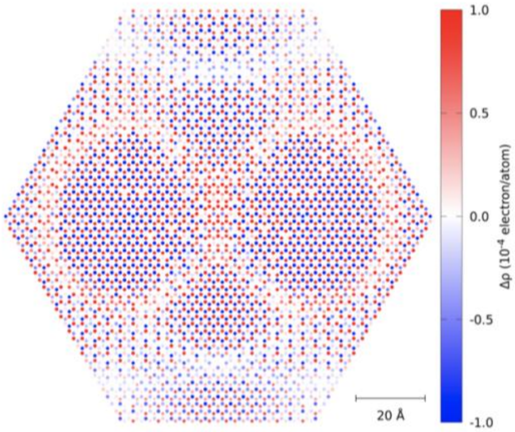


Figure 1: Electronic density variation in the presence of two local potentials. The calculations are performed using the prototypical version of the proposed package. The plot illustrates two sets of Friedel oscillations due to the two point defects. The sublattice asymmetry is evident.

References:

1. Noori, K., Quek, S. Y., Rodin, A. (2020) Hydrogen adatoms on graphene: The role of hybridization and lattice distortion, *Phys. Rev. B.*, **102**, 195416.
2. Noori, K., Biswas, H., Quek, S. Y., Rodin, A. (2020) Graphene-mediated interaction between hydrogen adsorbates, *Phys. Rev. B.*, **101**, 115421.

Ferroelectric domains and networks of piezoelectric domains in twistronic bilayers of transition metal dichalcogenides

Vladimir Falko [1,2]
[1] National Graphene Institute, University of Manchester, Booth Street East, Manchester M139PL, UK
[2] Henry Royce Institute for Advanced Materials, Oxford Road, Manchester M139PL, UK

Abstract:

Lattice reconstruction in small-angle-twisted bilayers of transition-metal dichalcogenide [1] gives rise to the neworks of domains with the energertically preferential stacking and domain walls, which are similar to dislocations in bulk crystals. In bilayers with the antiparallel (AP) orientation of the monolayers' unit cells, these domains correspond to the 2H stacking of the crystals with a honeycomb domain wall network hosting spots of piezoelectric charges and the corresponding quantum dots for electrons and hole at its sites with MM' and XX' stacking [1,2]. In bilayers with the parallel (P) orientation of the monolayers' unit cells, triangular-shape domains with a twin MX' and XM' stacking order form (similar to 3R stacking in bulk crystals), separated by partial screw dislocations network [1]. Such domains feature weak ferroelectric polarisation at the interface of the two monolayer crystals [3], which gives rise to their tunability - using the out-of-plane electric field which promotes domains with one energetically favourable polarisation (e.g., MX'). For such tunability, we find the threshold electric field at which parts of the partial domain wall dislocations merge into perfect (full) screw dislocation at the border of consecutive MX' domains, and, then, demonstrate the universal scaling of the overal domain wall shapes. We also find that electronic states at the conduction/valence band edges of the 3R stacking domains are layers polarised, leading to a large linear Stark shift for the interlayer excitons [4].

Finally, we use the result of the lattice relaxation analysis to describe the moire superlattice efects for electrons, holes and excitons in twisted bilayers, taking into account strain, interlayer hybridization of band-edge states, and piezo/ferroelectric potentials [5].

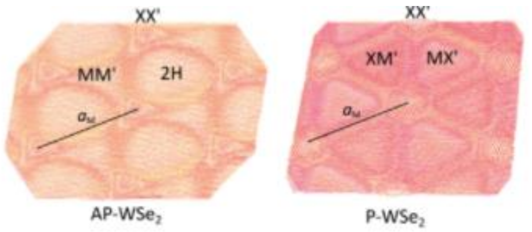


Figure 1. Examples of reconstructed twisted WSe2 bilayers with antiparallel (AP) and parallel (P) orientations of layers' unit cells. In-plane lattice reconstruction promotes the growth of hexagonal domains with 2H stacking for AP bilayers and triangular domains with XM′/XM′ stackings for P bilayers, whereas out-of-plane relaxation leads to bulging of energetically unfavorable XX′ stacking areas and domain walls ($\mathrm{Ab/A'_t}$ indicates which atoms in the bottom and top layers are vertically aligned, M stands for metal and X for chalcogen sites, and 2H coincides with MX′ stacking in AP structures).

References:

1. V Enaldiev, et al, Phys Re. Lett 124, 206101 (2020); A Weston, et al, Nature Nanotechn 15, 592 (2020).
2. V Enaldiev, et al, 2D Mater 8, 025030 (2020); F Ferreira, et al, Scientific Reports 11, 13422 (2021).
3. A Weston, et al, arXiv:2108.06489 .
4. H Sung, et al, Nature Nanotechn 15, 750 (2020).
5. F Ferreira, et al, Appl Phys Lett 118, 241602 (2021); S Magorrian, et al, Phys Rev B 104, 125440 (2021).

Scalable 2D materials for optoelectronic applications: Fabrication and device integration

G. Bacher [1,*], D. Andrzejewski[1], J. Mischke[1], U. Hutten[1], Y. Beckmann[1], H. Myja[1], A. Grundmann[2], H. Kalisch[2], M. Heuken[2], A. Vescan[2], W. Mertin[1], T. Kümmell[1]
[1] Werkstoffe der Elektrotechnik, University Duisburg-Essen, Duisburg, Germany
[2] Compound Semiconductor Technology, RWTH Aachen University, Aachen Germany

Abstract:
Atomically thin layers represent an exciting class of two-dimensional (2D) materials with unique properties, like e.g. high electrical conductivity combined with high transparency in case of graphene, or efficient light absorption and emission in case of transition metal dichalcogenides (TMDCs). Originally prepared by mechanical exfoliation for more basic scientific studies, developments in large area CVD growth techniques paved the path towards practical applications. In this contribution some of our recent efforts on scalable 2D materials grown by PECVD and MOCVD and their implementation in optoelectronic devices will be presented, both for graphene as well as TMDC layers.

Graphene has been grown by CVD in an AIXTRON Black Magic Pro reactor. In order to avoid decomposition and/or melting of the substrate, we reduce the process temperature by implementing a plasma-enhanced growth procedure first developed for Cu foils [1], and then adapted to both Ge [2] and GaN substrates. As a proof-of-concept, we demonstrate integration of directly grown graphene as a transparent electrode in GaInN/GaN light emitting devices. Our approach thus avoids contamination and process issues typical for transfer techniques. Strong lateral current spreading and a reduced turn-on voltage indicate the suitability of our concept [3].

Using a horizontal multiwafer AIXTRON MOCVD reactor, high quality films of both, MoS_2 as well as WS_2 monolayers have been realized. The potential of these ultrathin semiconductors for light emitting devices in the red spectral range is demonstrated by embedding MOCVD grown WS_2 monolayers in a vertical device design, where inorganic and organic support layers are used for electron and hole injection, respectively. Large area red electroluminescence stemming from the TMDC layer with a turn-on voltage as low as 2.5 V has been achieved for both, rigid [4] as well as flexible substrates [5]. The direct growth of a heterostructure comprising WS_2 and MoS_2 monolayers enables the fabrication of a photodetector without involving any transfer process. We demonstrate an enhancement of the responsivity by more than 5 orders of magnitude as compared to a single layer device, which we attribute to an efficient separation of optical generated electron-hole pairs at the WS_2-MoS_2 heterointerface [6].

Keywords: graphene, transition metal dichalchogenides, PECVD, MOCVD, scalability, light emitting devices, photodetectors, optoelectronic applications.

References:

1. Bekdüz, B. et al., Graphene growth through a recrystallization process in plasma enhanced chemical vapor deposition, *Nanotechnology* 29, 455603 (2018)
2. Bekdüz, B. et al., Direct growth of graphene on Ge(100) and Ge(110) via thermal and plasma-enhanced CVD, *Sci. Reports* 10, 12938 (2020)
3. Mischke, J. et al., Direct growth of graphene on GaN via plasma-enhanced chemical vapor deposition under N_2 atmosphere, *2D Materials* 7, 035019 (2020)
4. Andrzejewski, D. et al., Scalable large area p-i-n light emitting diodes based on WS_2 monolayers grown via MOCVD, *ACS Photonics* 6, 1832 (2019)
5. Andrzejewski, D. et al., Flexible large-area light-emitting devices based on WS_2 monolayers, *Adv. Opt. Mater.* 8, 2000694 (2020)
6. Hutten, U. et al., Transfer-free, scalable photodetectors based on MOCVD-grown 2D-heterostructures, *2D Materials* 8, 045015 (2021)

Boosting the properties of 2D materials with molecules: multi-responsive and high-performance based opto-electronic devices

Paolo Samorì
ISIS - Université de Strasbourg & CNRS, Strasbourg (France)

Abstract

Two dimensional materials exhibit exceptional physical and chemical properties which can be further enhanced and enriched via the controlled functionalization with molecules and (supra)molecular assemblies thereof yielding hybrid systems with ad hoc characteristics for applications in (opto)electronics, sensing and energy. Molecules can be designed and synthesized in order to physisorb or chemisorb onto 2D materials in a controlled fashion. [1]

In my lecture I will review our recent findings on the functionalization of 2D materials to engineer hybrid systems via:

- *physisorption* of molecular switches onto the two surfaces of scotch tape and CVD 2D semiconductors, following a Janus approach, to confer additional properties to WSe_2, rendering the 2D material-based transistors capable to respond to four different independent stimuli.[2]

- *chemisorption* of dithiolated molecules onto solution-processed semiconducting TMDs to simultaneously heal sulfur vacancies in metal disulfides and covalently bridge adjacent flakes, thereby promoting percolation pathways for charge transport, leading to a 10-fold increase in field-effect mobility, I_{ON}/I_{OFF} ratio, and switching times of liquid-gated transistors.[3]

Our modular strategies relying on the combination of 2D material with molecules offer a simple route to generate multifunctional coatings, foams and nanocomposites with pre-programmed properties to address key global challenges in electronics, sensing and energy applications.

Reference

[1] (i) M. Gobbi, E. Orgiu, P. Samorì, Adv. Mater. 2018, 30, 1706103. (ii) S. Bertolazzi, M. Gobbi, Y. Zhao, C. Backes, P. Samorì, Chem. Soc. Rev. 2018 47, 6845.

[2] (i) M. Gobbi, et al. Nat. Commun. 2018, 9, 2661. (ii) H. Qiu, et al., Adv. Mater. 2020, 32, 1907903. (iii) Y. Zhao, S. Bertolazzi, M. S. Maglione, C. Rovira, M. Mas-Torrent, P. Samorì, Adv. Mater. 2020, 32, 2000740. (iv) H. Qiu, S. Ippolito, A. Galanti, Z. Liu, P. Samorì, ACS Nano 2021, 15, 10668; (v) H. Qiu, M. Herder, S. Hecht, P. Samorì, Adv. Funct. Mater., 2021 in press (DOI: 10.1002/adfm.202102721)

[3] S. Ippolito, et al, Nat. Nanotech. 2021, 16, 592.

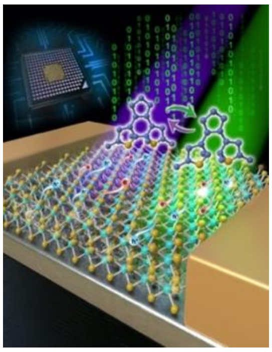


Figure 1: Optically switchable multilevel high-mobility FETs based on few-layer ambipolar WSe_2.

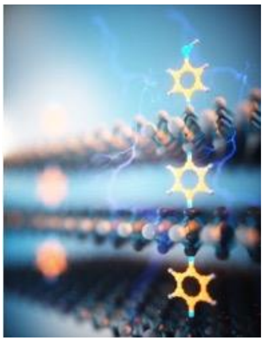


Figure 2: 1,4-benzenedithiol molecules healing sulfur vacancies in solution-processed MoS_2 and covalently bridging adjacent flakes, to create percolation pathways for the charge transport in FETs.

Beyond Graphene – How MXenes Expand the Range of 2D Materials for Electronics, Optics and Communication

Y. Gogotsi
A.J. Drexel Nanomaterials Institute, and Department of Materials Science and Engineering,
Drexel University, Philadelphia, PA 19104, USA

Abstract:

Discovery of new materials provides moments of inspiration and shifts in understanding, shaping the dynamic field of materials science. Following the graphene breakthrough, many other 2D materials emerged. Although many of them remain subjects of purely academic interest, others have jumped into the limelight due to their attractive properties, which have led to practical applications. Among the latter are 2D carbides and nitrides of transition metals known as MXenes [1]. The family of MXenes has been expanding rapidly since the discovery of Ti_3C_2 in 2011 [2]. More than 30 different stoichiometric MXenes have been reported, and the structure and properties of numerous other MXenes have been predicted. Moreover, the availability of solid solutions on M and X sites, multi-element high-entropy MXenes, control of surface terminations, and the discovery of out-of-plane ordered double-M *o*-MXenes (e.g., Mo_2TiC_2), as well as in-plane ordered *i*-MAX phases and their *i*-MXenes offer a potential for producing dozens of new distinct structures. This presentation will describe the state of the art in the manufacturing of MXenes, their delamination into single-layer 2D flakes and assembly into films, fibers and 3D structures. Synthesis-structure-properties relations of MXenes will be addressed on the example of Ti_3C_2. The versatile chemistry of the MXene family renders their properties tunable for a large variety of applications. In particular, the interaction of MXenes with electromagnetic waves can be controlled via their composition and structure. Many MXenes offer high electronic conductivity and outstanding electromagnetic interference shielding. They can also be used in telecommunication, energy, medical and electronic device applications.

Keywords: MXene, 2D material, carbide, communication, optics, electronics.

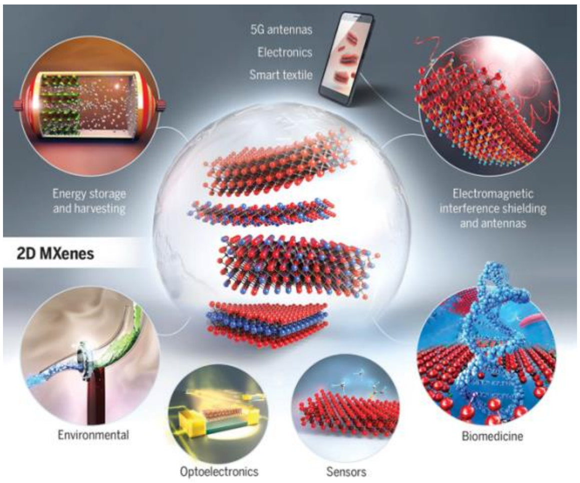


Figure 1: Structure and applications of 2D carbides and nitrides (MXenes). The large number of MXene compositions having structures with three, five, seven, or nine atomic layers containing one or two kinds of metal atoms and various surface terminations (−F, =O, −Cl, −Br, etc.) have shown promising optoelectronic, mechanical, and electrochemical properties. They have found use in a wide range of applications ranging from energy storage and harvesting to catalysis, water purification and desalination, electromagnetic interference shielding, communication, optics, electronics, plasmonics, sensors, actuators, composites, and medicine [1].

Reference:

1. A. VahidMohammadi, J. Rosen, Y. Gogotsi, The World of Two-Dimensional Carbides and Nitrides (MXenes), *Science*, 372, eabf1581 (2021)
2. M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J.-J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2, *Advanced Materials*, 23, 4248-4253 (2011)

Spintronics in 2D Van der Waals materials

Bart van Wees[1*], T.S. Ghiasi[1], A.A. Kaverzin[1], A. H. Dismukes[2], D.K. de Wal[1], J. Ingla Aynes[1], P.J. Blah[1], and X.Roy[2]

[1]Zernike Institute for Advanced Materials, University of Groningen, The Netherlands
[2]Department of Chemistry, Columbia University, New York, NY, USA
*b.j.van.wees@rug.nl

Abstract:
I will introduce spintronics in graphene, highlighting the elementary experimental techniques, using ferromagnetic electrodes for spin injection and spin detection, and applied magnetic fields to control the spin direction by Hanle spin precession. This has shown graphene as an ideal long range carrier of electronic spins [1]. I will then give examples how (strongly anisotropic) spin relaxation can be induced in graphene using proximity to semiconducting transition metal dichalcogenides (TMDs) with strong spin orbit interaction [2]. In similar graphene/TMD systems it was shown that interconversion of spin and charge currents can be achieved, using proximity induced spin Hall and Rashba-Edelstein mechanisms and their reciprocals [3].

As the main subject I will discuss how graphene can be made magnetic by the proximity of the layered Van der Waals antiferromagnet CrSBr. We showed that a strong exchange field of 170T, corresponding to a spin splitting of about 10 meV, is induced in the graphene, and modifies the electronic bandstructure [4]. Non-local and local charge and spin transport measurements have shown that in this system a spin polarization of the conductivity of 14 % is obtained, similar in value to that in conventional 3D metallic ferromagnets. In addition the proximity induced spin polarization has resulted in a spin dependent Seebeck effect, where a thermal gradient induces a pure spin current due to the spin dependent values for the Seebeck coefficients [4].

I will discuss ongoing experiments where we aim at controlling the magnitude, as well as sign, of the spin polarization in the magnetic graphene by gate tuning the carrier density and Fermi energy. This will also allow to make new device functionalities such as lateral spin valve devices based on magnetic graphene, and fully spin polarized edge channels in high magnetic fields. Finally I will discuss how we intend to use these systems to make a fully spin polarized 2D system, a two dimensional spin gas.

Keywords: spintronics, graphene, 2D materials, heterostructures, spin orbit interaction, exchange interaction, magnetism, proximity effects

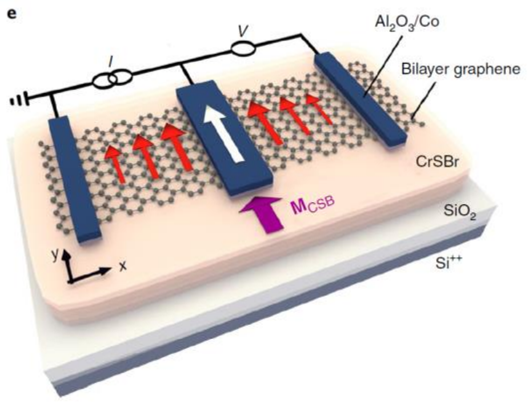


Figure 1: Device layout for studying electrical and thermal spin current generation by magnetic graphene. The proximity of the layered antiferromagnet induces a strong exchange spin splitting in the bilayer graphene. The resulting spin polarization of the conductivity and the spin dependent Seebeck coefficients are studied by spin injection and detection, as well as local heating by conventional Co ferromagnetic electrodes (from ref. 4)

References:

1. Han, W., Kawakami, R.K., Gmitra, M., Fabian, J., (2014) *Nature Nanotechn.* 9, 794.
2. Ghiasi, T.S., Ingla Aynes, J., Kaverzin, A.A., Van Wees, B.J., (2017) *Nano Lett.* 17.12, 7528.
3. Ghiasi, T.S., Kaverzin, A.A., Blah, P.J., Van Wees, B.J., (2019) *Nano Lett*. 19.9, 5959.
4. Ghiasi, T.S., Kaverzin, A.A., Dismukes, De wal, D.K., Roy, X., Van Wees, B.J., (2021) Nature Nanotechn. 16, 788.

Disclosing the Covalent Functionalisation of Graphene by PAMAM Dendrimers and their Applications by Molecular Simulations

M. Natália D. S. Cordeiro [1*], Vasumathi Velachi [1], Mounika Gosika [2], Prabal K. Maiti [2]
[1] LAQV@REQUIMTE/Dept. Chemistry and Biochemistry, University of Porto, Porto, Portugal
[2] Condensed Matter Theory, Department of Physics, Indian Institute of Science, Bangalore, India

Abstract:

Functionalisation of graphene and its derivatives (e.g. graphene oxide) with polymers is receiving much attention lately, owing to their potential applications in CO_2 or heavy metal adsorption, energy storage, biosensors, and drug delivery. Among other, hyper-branched such as poly-(amidoamine) (PAMAM) dendrimers are highly reactive because of the presence of a large number of terminal functional groups, and so, they are particularly suited for functionalisation of graphene. Covalent functionalisation of graphene is indeed a very promising strategy due to the formation of stronger bonds that give rise to a stable nanocomposite for various applications. Two major grafting approaches are employed for covalently grafting the polymers onto solid surfaces, namely *grafting-from* and *grafting-to* (Fig.1). Even though there are several experimental studies on the covalent functionalisation of graphene by dendrimers and its application, computational studies are lacking, which explore the impact of changing the grafting approach or binding location. In this communication we move a step forward and present results of molecular dynamics (MD) simulations regarding the covalent functionalisation of graphene with PAMAM dendrimer by the two grafting approaches (from and to) for different binding locations (*top*, *edge*, and *top-edge*). The effect of the grafting approach used, the binding site, the surface area, and the dispersion are analysed in detail. In addition, the possible cytotoxicity of the dendrimer functionalised graphene is investigated by analysing its interactions with a typical lipid bilayer. These MD results pave the way for a more complete theoretical understanding of the key factors governing the covalent functionalisation of graphene and its implications on graphene's dispersion and cytotoxicity, which could lead to a development in the fabrication of graphene-based devices and their applications.

Keywords: dendrimers, graphene, covalent functionalization, grafting-from *vs.* grafting-to approaches, dispersion, graphene-based devices, biomedical applications.

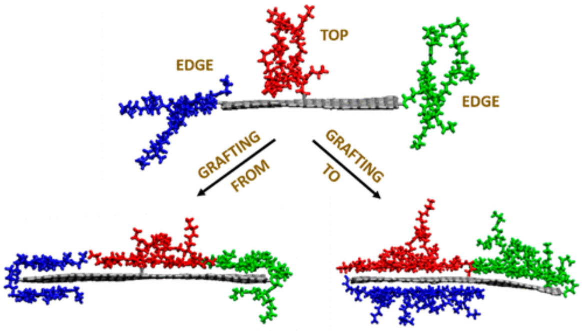


Figure 1: Figure illustrating typical equilibrated snapshots of the graphene-dendrimer composites corresponding to various binding locations of the dendrimer from the two grafting approaches, considered in this study.

References:

1. Cheng, C., Li, S., Thomas, A., Kotov, N.A., Haag, R. (2017) Functional Graphene Nanomaterials Based Architectures: Biointeractions, Fabrications, and Emerging Biological Applications, *Chem. Rev*. 117, 1826-1914.
2. Astruc, D., Boisselier, E., Ornelas, C. (2010) Dendrimers Designed for Functions: From Physical, Photophysical, and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular Electronics, Photonics, and Nanomedicine, *Chem. Rev*. 110, 1857-1959.
3. Englert, J., Dotzer, C., Yang, G. et al. (2011) Covalent bulk functionalization of graphene. *Nature Chem*. 3, 279-86.
4. Gosika, G., Velachi, V., Cordeiro, M.N.D.S., Maiti, P.K. (2020) Covalent Functionalization of Graphene with PAMAM Dendrimer and Its Implications on Graphene's Dispersion and Cytotoxicity*ACS Appl. Polym. Mater*. 2, 3587-3600.

Laser Induced Backwards Transfer (LIBT) of graphene onto glass.

M. Praeger [1,*], R. W. Eason [1], B. Mills [1]

[1] Optoelectronics Research Centre, University of Southampton, Southampton, U.K.

Abstract:

Graphene growth is typically optimized for uniformity over relatively large areas; however, this can place undesirable limitations on the design of graphene-based devices and can mandate the use of additional lithographic processing steps. Localized transfer of graphene can therefore offer significant benefits, permitting greater freedom in device design thereby enabling new applications.

We present results obtained using a laser transfer method that is capable of localized deposition of graphene onto transparent receiver materials such as glass (using just a single fs laser pulse per deposited structure). In this method (laser induced backwards transfer, LIBT [1-3]) a pulsed laser beam is focused through the receiving substrate and onto the donor substrate (hence the requirement for the receiver to be transparent at the incident laser wavelength). In this case the receiver is a microscope cover glass, which is held in close contact with the donor during LIBT. The donor is a nickel-coated glass slide upon which large-area monolayer graphene is transferred via the floating film technique with the aid of a PMMA support layer that is subsequently dissolved. The focused laser pulse is transmitted through the graphene layer and is absorbed within the metal layer of the donor causing rapid, localized, thermal expansion (a shockwave). This locally ejects the graphene from the donor surface (only where the laser was focused) and transfers it to the receiver substrate. In this manner, microscale patterning of graphene on the receiver substrate is achieved.

Additionally, we present details of spatial beam modulation via a digital micromirror device (DMD, [4, 5]) which allows the shape and size of the deposited graphene to be precisely computer controlled in the micron range. This innovation could facilitate rapid prototyping of graphene-based devices, allowing numerous design variations to be tested quickly and without requiring purchase of multiple, costly, lithographic masks. This work extends on previous results obtained with 800nm laser light [6] by using an optical parametric amplifier (OPA) emitting at 1650nm. This wavelength allows development of the LIBT process with glass receiver substrates prior to translation to our final target; LIBT through and onto silicon.

The presence of graphene on a surface creates a slight change in optical reflectance and so it is often possible (although difficult) to observe the presence of localized deposits of graphene via optical microscopy. We have developed image processing methods (with contrast enhancement and image segmentation steps) that greatly simplify the identification of graphene-coated regions. These methods have been evaluated using Raman microscopy and have proved to be an accurate and convenient tool (see Figure 1) which we believe may be of interest to other researchers in this field.

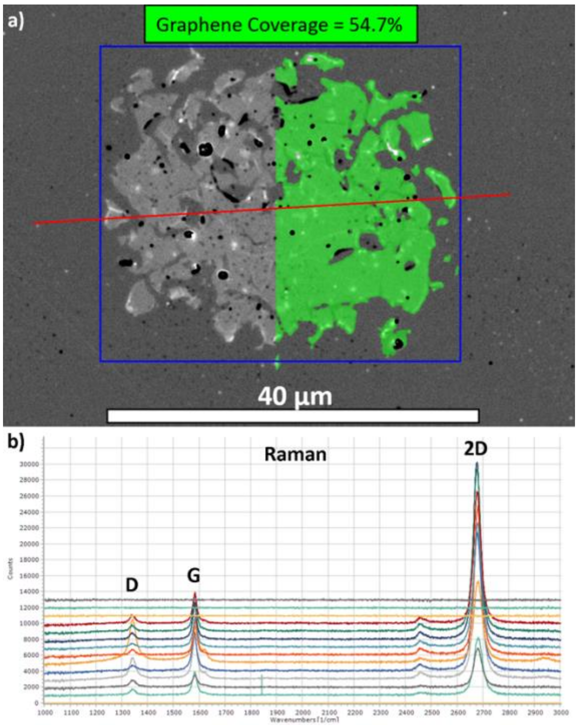


Figure 1: a) Contrast enhanced optical microscope image (taken using a 100x objective) showing a localized deposit of graphene on a glass substrate. The blue box shows the approximate laser beam shape, the green color on the right is automatically added via image segmentation to label regions of the image that contain graphene. b) Accuracy of the image segmentation was confirmed via Raman spectroscopy with multiple scans made along the red line shown in a).

Keywords: laser, deposition, transfer, LIBT, LIFT, graphene, 2D materials, image processing, device fabrication.

References:

1. Sakata, H., Chakraborty, S., Wakaki, M. (2012) Patterning of Bi2O3 films using laser-induced forward and backward transfer techniques. *Microelectron. Eng.* 96, 56-60.
2. Feinaeugle, M., Heath, D.J., Mills, B., Grant-Jacob, J.A., Mashanovich, G.Z., Eason, R.W. (2016) Laser-induced backward transfer of nanoimprinted polymer elements. *Appl. Phys. A-Mater. Sci. Process.* 122(4), 5.
3. Logotheti, A., Zacharatos, F., Makrygianni, M., Zergioti, I. (2020) Laser Induced Backward Transfer of ultra-thin metal structures. *Appl. Surf. Sci.* 512, 145730.
4. Mills, B., Feinaeugle, M., Sones, C.L., Rizvi, N., Eason, R.W. (2013) Sub-micron-scale femtosecond laser ablation using a digital micromirror device. *J. Micromech. Microeng.* 23(3), 8.
5. Mills, B., Grant-Jacob, J.A., Feinaeugle, M., Eason, R.W. (2013) Single-pulse multiphoton polymerization of complex structures using a digital multimirror device. *Opt. Express*. 21(12), 14853-14858.
6. Praeger, M., Papazoglou, S., Pesquera, A., Zurutuza, A., Levi, A., Naveh, D., Zergioti, I., Eason, R.W., Mills, B. (2020) Laser-induced backward transfer of monolayer graphene. *Appl. Surf. Sci.* 533, 147488.

Transfer of large−area wrinkled graphene onto polymeric substrates

Prashant Narute [1, 2,*], Rakesh S. Sharbidre [2], Chang Jun Lee [2, 3], Byong Cheon Park [2], Hyun-June Jung [4], Jae-Hyun Kim [5], Seong-Gu Hong [1, 2]

[1] Department of Nano Science, University of Science and Technology, Daejeon 34113, Republic of Korea.
[2] Interdisciplinary Materials Measurement Institute, Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea.
[3] Department of Mechanical Engeering, Chonnam National University, Gwangju 61186, Republic of Korea.
[4] Center for Advanced Meta-Materials, Daejeon 34103, Republic of Korea.
[5] Nano-Convergence Mechanical System Resrarch Division, Korea Institute of Machinary & Materials, Daejeon 34103, Republic of Korea.

Abstract:
Wrinkle engineering of graphene is demonstrated as an effective tool to alter physical properties, and exhibits potential applications in flexible and stretchable electronics, surface modifications, tunable optical transmittance, and energy storages. Therefore, efforts have been made to construct controlled and ordered wrinkled graphene (WGr) corrugations. In general, the employed WGr pattern is used with deformed substrate (the substrate which offers wrinkle creation on external stimulant) for end-use applications. Its usability, however, is limited by the poor transferability onto other substrates. Herein, we report a roll-based, damage-free, and clean transfer approach that enables the transfer of large-area wrinkled graphene onto polymeric substrates without compromising the integrity of wrinkle structure by exploiting a water-soluble sacrificial interface layer. Fabrication technique consists imidazole-assisted simultaneous etching and *p*-type doping of chemical vapor deposited graphene, which enhance both interfacial adhesion and electrical conductivity of graphene. Imidazole enables the use of a roll-based transfer process for fabricating mechanically robust and highly transparent conductive multilayer graphene on a thermally-shrinkable polystyrene (PS) substrate coated with a water-soluble poly(4-styrenesulfonic acid) (PSS) sacrificial interface layer. The PS substrate undergo thermal contraction against external stimuli and leading to the wrinkle formation on compliant PSS as well as graphene layer. As the compliant PSS interface layer provide the conformal contact between graphene and PS, controlled and conformal wrinkling with deterministic wrinkle-feature size is achieved. Transfer of WGr onto the target polymer (ethylene vinyl acetate/Polyethylene terephthalate (EVA/PET) and poly(dimethyl siloxane) PDMS) substrates was done by separating wrinkled graphene from the PS substrate. Here, readily water-soluble PSS made a process of separating wrinkled graphene from the PS substrate easy by circumventing the difficulty of removing the PS substrate, which improved the transferability of wrinkled graphene and made the transfer process solvent-free and clean. Proximal contact between wrinkled graphene and target substrate secured by the melting followed by encapsulation of EVA, and forming an extended, interlock interface by pre-cured PDMS liquid permeate into the gaps of wrinkled microstructure. These features offer geometric confinement and prevent the elastic recovery of graphene wrinkle during transfer process and while separating from the PS substrate; thus, preserving the structural integrity of graphene wrinkle, conformal interface and mechanical stability.Transferred wrinkled graphene has shown optical transmittance (~87%), sheet resistance (146 Ω/sq.), and superior stretchability (~100%) with excellent electromechanical stability tested for hundred cycles, making it suitable for transparent flexible electronics

Keywords: Wrinkled graphene, transfer of wrinkled graphene, flexible electronics, stretchability, roll-based transfer process, thermally shrinkable polystyrene

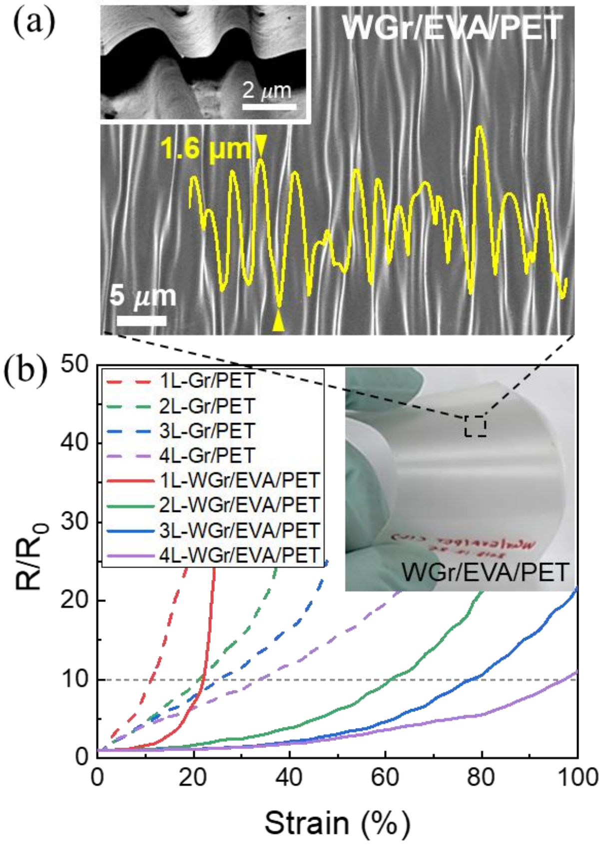


Figure 1: (a) Showing the SEM image, cross sectional view (inset), and height profile (yellow line) of transferred wrinked graphene onto target polymer substrate (EVA/PET). (b) Illustrating the improvement in electromechanical peroformance of wrinkled graphene (solid line) compaired to that of flat graphene (doted line). Inset in (b) is the photograph of centimeter-scale wrinkled graphene transferred onto EVA/PET substrate.

References:

1. Wenjun C., Xuchun G., Leilei Y., Hai Z., Zikang T. (2019), Wrinkling of two-dimensional materials: methods, properties and applications, *Nanoscale Horiz.* 4, 291-320

Chemical-Free Acoustomicrofluidic Synthesis of Ultrathin Pristine $Ti_3C_2T_z$ MXene Nanosheets and Quantum Dots

H. Alijani [1,*], A. R. Rezk [1], M. M. Khosravi Farsani [1], H. Ahmed [1], J. Halim [2], P. Reineck [3],
B. J. Murdoch [4], A. El-Ghazaly [2], J. Rosen [2], L. Y. Yeo [1]
[1] Micro/Nanophysics Research Laboratory, RMIT University, Melbourne, VIC 3000, Australia
[2] Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM),
Linköping University, Linköping SE-58183, Sweden
[3] ARC Centre of Excellence for Nanoscale BioPhotonics, School of Science,
RMIT University, Melbourne, VIC 3000, Australia.
[4] RMIT Microscopy & Microanalysis Facility, STEM College,
RMIT University, Melbourne, VIC 3000, Australia

Abstract:

The conversion of layered transition metal carbides and/or nitrides (MXenes) into zero-dimensional structures with thicknesses and lateral dimensions of a few nanometers allows these recently discovered materials with exceptional electronic properties to exploit the additional benefits of quantum confinement, edge effects, and large surface area. Conventional methods for the conversion of MXene nanosheets and quantum dots, however, involve extreme conditions such as high temperatures and/or harsh chemicals that, among other disadvantages, lead to significant degradation of the material as a consequence of their oxidation. Herein, we show that the large surface acceleration—on the order of 10 million *g*'s—produced by high-frequency (10MHz) nanometer-order electromechanical vibrations on a chipscale piezoelectric substrate is capable of efficiently nebulising, and consequently, dimensionally reducing a suspension of multilayer $Ti_3C_2T_z$ (MXene) into predominantly monolayer nanosheets and quantum dots whilst, importantly, preserving the material from any appreciable oxidation. As an example application, we show that the high purity MXene quantum dots produced using this room-temperature chemical-free synthesis method exhibit superior performance as electrode materials for electrochemical sensing of hydrogen peroxide compared to the highly-oxidised samples obtained through conventional hydrothermal synthesis. The ability to detect concentrations as low as 5nM is a ten-fold improvement to the best reported performance of $Ti_3C_2T_z$ MXene electrochemical sensors to date.

Keywords: $Ti_3C_2T_z$ MXene, quantum dots, nanosheets, acoustic waves, H_2O_2 sensing.

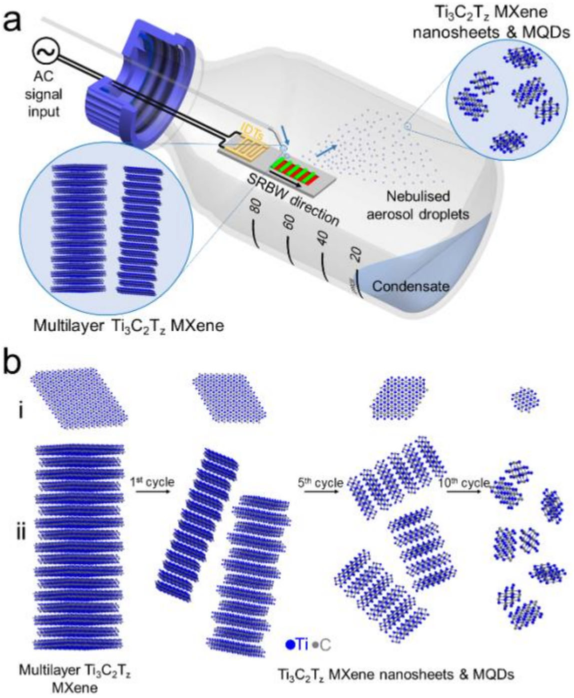


Figure 1: (a) Schematic illustration of the experimental setup in which a multilayer $Ti_3C_2T_z$ MXene sample is continuously delivered to the surface reflective bulk waves (SRBW) device, atop which it nebulises to form aerosol droplets of delaminated and cleaved $Ti_3C_2T_z$ which condense within the glass bottle enclosure. (b) Successive renebulisation of the condensate collected over many cycles is observed to (i) laterally cleave, and, (ii) delaminate the sample into progressively smaller and thinner MXene nanosheets and MQDs.

References:

1. Naguib, M., *et. al.* (2011). Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2. *Adv. Mat.*, 23(37), 4248-4253.
2. Alijani, H., *et. al.* (2021). Acoustomicrofluidic Synthesis of Pristine Ultrathin $Ti_3C_2T_z$ MXene Nanosheets and Quantum Dots. *ACS nano*.

Laser Induced Forward Transfer of Graphene for flexible touch sensors

Adamantia Logotheti[1], Filimon Zacharatos[1], Simeon Papazoglou[1], Amaia Pesquera[2], Amaia Zurutuza[2], and Ioanna Zergioti[1*]

1. School of Applied Mathematics and Physical Science, National Technical University of Athens, 15780, Zografou, Greece
2. Graphenea Headquarters, Paseo Mikeletegi 83, 20009 - San Sebastián, Spain
Corresponding author's email: zergioti@central.ntua.gr

Abstract: 2D materials have been increasingly incorporated in flexible electronics and sensors over the past few years [1]. Despite the impressive developments 2D materials have recently showcased, there are still challenges related to their deposition and integration, which impede their further advancement. To this end, the intact and high-resolution deposition of 2D materials is of great importance. Laser Induced Forward Transfer (LIFT) has been reported as a reliable, high resolution and digital fabrication tool for flexible electronics, sensors and optoelectronics [1]. In this paper, we will demonstrate the fabrication process of a Graphene enabled, flexible touch sensor employing LIFT. More specifically, we will report on the fabrication process and the performance characterization, highlighting the advantages of LIFT, over more conventional, top-down processes. LIFT allows for the controllable transfer of Graphene arrays with a footprint of 1 mm^2, and overall form factors suitable for electrodes in parallel plate capacitor configurations. As can be seen in Fig. 1, the touch sensor consists of an array of parallel plate capacitors, comprising Graphene as the top electrode, PDMS as the dielectric and Ag nanoparticles (NPs) as the bottom electrodes. Both the top and the bottom electrodes were fabricated using LIFT, in successive printing steps (Fig 2). In addition, for the needs of electrical characterization, micro-pads and interconnections made of silver paste were printed by LIFT. The transfer of single layers of Graphene pixels was confirmed by Raman and SEM characterization. The preliminary capacitance measurements of the touch sensor indicated a 2-4 pF capacitance at 1 MHz and 1 Volt. Variations of the dielectric's thickness induced by applied tensile or compressive stress are expected to result in commensurate variations of the measured capacitance. Overall, the results show significant promise for the development of a sensitive Graphene-based touch sensor with thin, flexible and lightweight form factors.

Keywords: Graphene electrodes, 2D materials, LIFT technique, flexible electronics, touch sensor, flexible capacitor

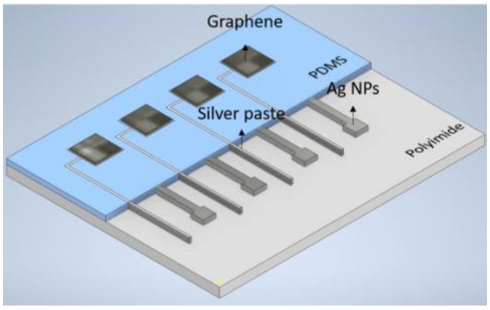


Figure 1: Figure illustrating the design of thetouch sensor with top electrodes : Graphene arrays connected with siver paste, dielectric: PDMS, bottom electrodes : Ag NPs , flexible substrate : Polyimide

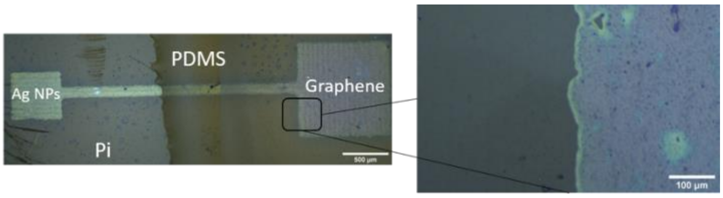


Figure 2: Microscopy photo of transferred Graphene (Top electrode) with LIFT on PDMS/Bottom electrode.

References:

1. Berger, Ch., Phillips, R., Centeno, A., Zurutuza, A., Vijayaraghavan, A., (2017), Capacitive pressure sensing with suspended graphene-polymer heterostructrure membranes, *Nanoscale*, 9, 17439
2. Koritsoglou, O., Theodorakos, I., Zacharatos, F., Makrygianni, M., Kariyapperuma D., Price, R., Cobb, B., Melamed, S., Kabla, A., De la Vega, F., Zergioti. I., (2019) Copper micro-electrode fabrication using laser printing and laser sintering processes for on-chip antennas on

flexible integrated circuits, *Opt. Mater. Express*, 9, 3046-3058

Memristive Graphene/Ionic Liquid Devices: Characterization and Demonstration of Associative Learning

I. Köymen[1,*], S. Liu[2], S. Ergöktaş[2], C. Kocabaş[2]
[1] Department of Electrical and Electronics Engineering, TOBB University of Economics and Technology, Ankara 06560, Turkey
[2] Department of Materials, National Graphene Institute, University of Manchester, M13 9PL, Manchester, United Kingdom

Abstract:

Flexible and biocompatible memristive are particularly attractive for bioelectronic systems due to the interest in improving computing capabilities and the motivation to interface electronics with biological systems including drug delivery, neural interfaces and biosensors [1]. Structures made of more unorthodox, organic material can address different issues due to their characteristics: flexibility, conformability, biocompatibility and simple and low-cost fabrication [2,3].

It has been observed that gating Graphene/Ionic Liquid (IL) devices leads to the formation of an electrical double layer (a thin layer of ions with a thickness of a few nanometers) at the graphene/IL interface [4] due to the local potential difference which also controls the local conductivity. This structure provides a memristive mechanism based on a dynamic p-n junction formation along the channel as shown in Figure 1. Motivated by this memristive behaviour, graphene/IL devices of two distinct topologies were assembled with the aim of demonstrating memristive behavior and associative learning.

This work investigates memristive properties of flexible graphene/ ionic liquid devices on polymer substrates. The I-V characteristics of these novel devices and switching mechanism are investigated. Two distinct topologies (single input, single output and double input, single output) of devices are manufactured and tested to mimic conditioning. It is observed that the application of voltage pulse trains of both positive and negative polarities increases the device conductance and allows larger currents to pass after repetitive excitation. This characteristic was exploited to condition devices and emulate associative learning.

Keywords: memristor, graphene, ionic liquid, associative learning, neuromorphic applications

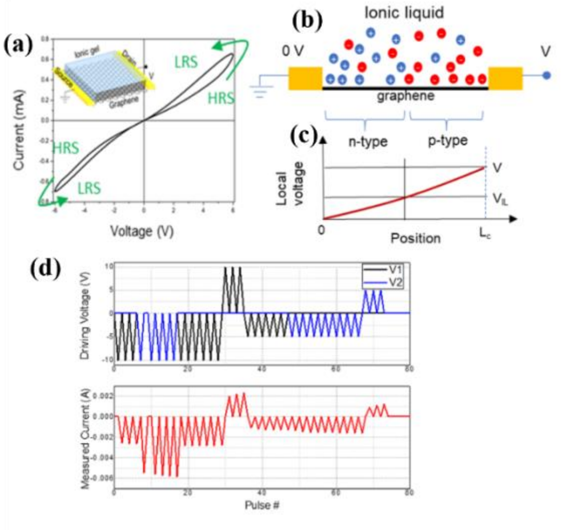


Figure 1 depicting (a) Graphene/IL device memristive pinched hysteresis loop, (b) representation of a dynamic p-n junction formed on the graphene channel, variation of the local potential redistributes ions in the electrolyte and forms dynamic doping on graphene, (c) Variation of the local potential along the channel under a bias voltage, (d) response of a 2-input terminal 1-output terminal flexible polymer substrate graphene/IL device to voltage pulses.

References:

1. P. Gkoupidenis, D. A. Koutsouras and G. G. Malliaras, “Neuromorphic device architectures with global connectivity through electrolyte gating,” Nature Communications, vol. 8, p. 15448, 2017.
2. Y. Kim, A. Chortos, W. Xu, Y. Liu, J. Y. Oh, D. Son, J. Kang, A. M. Foudeh, C. Zhu, Y. Lee, S. Niu, J. Liu, R. Pfattner, Z. Bao and T.-W. Lee, “A bioinspired flexible organic artificial afferent nerve,” Science, vol. 360, no. 6392, pp. 998-1003, 2018.
3. N. Raeis-Hosseini and J. Rho, “Solution-Processed Flexible Biomemristor Based on Gold-Decorated Chitosan,” *ACS Appl. Mater. Interfaces*, 2021.
4. E. O. Polat and C. Kocabas, “Broadband Optical Modulators Based on Graphene Supercapacitors,” *Nano Letters,* vol. 13, no. 12, pp. 5851-5857, 2013.

Dirac nodal-loops in two-dimensional Cu$_2$Si

M. Cameau [1,2], C.-H. Chen [3], A. Huang [3], R. Ishibiki [4], T. Kondo [4], H.-T. Jeng [3,5,6], I. Matsuda [7] , M. D'angelo [1].
[1] Institut des nanosciences de Paris, Sorbonne Université, France
[2] Institut de minéralogie, de physique des matériaux et de cosmochimie, Sorbonne Université, France
[3] Department of Physics, National Tsing Hua University, Taiwan
[4] Faculty of Pure and Applied Sciences, University of Tsukuba, Japan
[5] Physics Division, National Center for Theoretical Sciences, Taiwan
[6] Institute of Physics, Academia Sinica, Taiwan
[7] Institute for Solid State Physics, University of Tokyo, Japan.

Abstract:

With the discovery of Dirac nodal-lines and nodal-loops (DNL), the notion of Dirac point has been extended to lines and loops in momentum space. As for Dirac cones, the energy dispersion of a DNL is linear around the band crossing, but these systems have symmetry-protected drumhead-like surface states with narrow band dispersions, giving rise to a high density of states near the Fermi level.

The interest of fabricating such materials is twofold. Firstly, because they hold great promises for applications, especially for nano-electronic devices made from heterostructures. Secondly, because their topological states are directly observables by angle-resolved photoemission spectroscopy (ARPES), making them ideal platform to study topology-related issues.

While 3D materials were the first in which DNL fermions were founds, DNL have now been predicted in many 2D systems with monolayer hexagonal lattices, honeycomb-kagome lattices, or monolayer transition metal-group VI compounds. However, their experimental realization appears rather challenging. The first 2D DNL were experimentally evidenced in Cu$_2$Si. It is composed of a honeycomb Cu lattice and a triangular Si lattice; both coplanar (see *Fig 1*). In 2017, Feng *et al.* showed that when prepared on a Cu(111) substrate, ARPES measurements revealed two concentric DNL close to the Fermi level and centred on the high-symmetry point Γ, in agreement with first principle calculations [1]. These nodal lines are shown to be protected by mirror crystalline symmetry. The weak interaction between the Cu substrate and the monolayer allowed for the preservation of those symmetries, and thus of the nodal-line fermions.

In the optics of realizing electronic devices, many challenges are yet to overcome: the instability of the DNL monolayer outside of the ultra-high vacuum where it is formed, and the choice of a proper non-conductive and decoupled substrate appear to be the firsts no tackle. Roth *et al.* reproduced the results of Cu$_2$Si on Cu(111), and showed by ARPES that the Cu$_2$Si monolayer could be encapsulated by a graphene sheet while keeping intact the DNL [2]. For the DNL states to exist, it is necessary for the 2D layer to be as decoupled from the substrate as possible. We will present here how the choice of substrate can induce drastic changes in the electronic structure. We investigated the properties of Cu$_2$Si prepared on a Si(111) semiconductor substrate, more relevant for electronic devices, and showed that the electronic structure was substantially modified due strong coupling between the out-of-plane orbitals of the monolayer and the substrate [3].

Keywords: Dirac nodal-line, nodal-loop, angle-resolved photoelectron spectroscopy, two-dimensional monolayer.

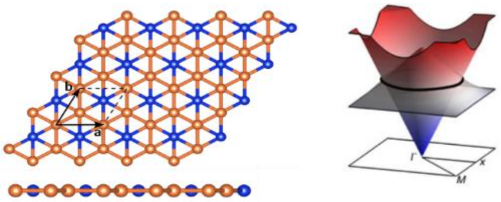


Figure 1: **Left:** top and side-view representations of Cu$_2$Si, with Cu atoms in orange and Si atoms in blue. The lattice vectors are represented. **Right:** A Dirac nodal loop (black circle) formed from the crossing of two bands, from W. Gao, *et al.* Nat. Com. **9,** 950 (2018).

References:

1. B. Feng *et al.*, (2017) "Experimental realization of two-dimensional Dirac nodal line fermions in monolayer Cu2Si," *Nature Communications*, vol. 8, 1, 1007.
2. S. Roth *et al.*, (2019) "The growth and band structure of a graphene-encapsulated two-dimensional nodal line semimetal: Cu$_2$Si", *Elec. Struct.* 1, 1, 04001.
3. M. Cameau et al., (2019) "Electronic structure of a monoatomic Cu$_2$Si layer on a Si(111) substrate", *Phys. Rev. Materials,* vol. 3, 4, 044004.

Graphene-coated E-textiles based on hydrophilic and hydrophobic fabrics

B. Meskini [1,*], T. Bashir [1,2], N-K. Persson [1]

[1] Swedish School of Textiles, Polymeric E-textiles, University of Borås, S-501 90 Borås, Sweden
[2] Swedish Centre for Resource Recovery, University of Borås, S-501 90 Borås, Sweden

Abstract:
Smart textile has been studied in myriad of applications such as medical, bio-sensing, communication, energy harvesting and storage, and as important components for exploring this area; flexible and conductive materials have drawn the attention. Graphene is one of the promising materials due to the potential of adding electrical properties while only having a low negative impact on textile properties. Then graphene and its different routes for deposition are highly interesting to study. The aim of this research is to build a platform for tailor making the electrical properties of graphen coated fabrics and E-textiles in general complementing earlier efforts (1) on non-metalled based conductity. It is central to know what substrates that are suitable to use for such e-textiles.

For this, two types of fabrics have been used, woven viscose and wowen polyester, to be regarded as hydrophobic and hydrophilic, respectively. A dip-coating in graphene oxide (GO) dispersion has been applied subsequently to an alkali and chitosan treatment of both fabrics. The alkali treatment has been made using sodium hydroxide (NaOH) to ensure hydrophilicity of the textile material for more GO absorption, whereas the chitosan treatment has been performed, giving the textile surface positive charges, to make a further electrostatic attraction between textile materials and the negatively charged graphene oxide (GO). The hydrophilicity and the surface charge have been tested through water contact angle and Zeta potential characterisation, respectively. Furthermore, chemical reduction of GO to reduced graphene oxide (rGO) has been elaborated. The chemical reduction of the coated samples included the investigation of two reducing agents; tannic acid and sodium dithionite, where the influence of two parameters, the concentration and the process time, have been studied. Two concentrations (50 and 100 mM), and three process times (15, 30 and 60 minutes for sodium dithionite reduction and 4, 8 and 14 hours for tannic acid reduction) have been applied. The samples were characterised through resistance and colour measurements. Results showed that the treatment (alkali+ chitosan) has affected both fabrics properties showing a significant difference in resistance between treated and non-treated samples. Moreover, the investigation of both reducing agents alongside with the concentration and process time in the chemical reduction of GO, has shown that using sodium dithionite as reducing agent exhibits better electrical properties, results also showed that by increasing time and/or concentration, the resistance decreases. The lowest resistance that has been measured for both viscose and polyester are around 2 kΩ and 4 kΩ respectively, these resistances have been achieved by reducing the GO-coated samples using 100 mM of sodium dithionite solution as reducing agent for 60 minutes.

This opens up for doping of the rGO-coated samples with a spectrum of appplications.

Keywords: graphene oxide, reduction, smart textiles, e-textiles, fabrics, textiles, chitosan, alkali.

References:

1. T. Bashir, N-K. Persson, M. Skrifvars (2017) High-strength electrically conductive fibers: Functionalization of polyamide, aramid and polyester fibers with PEDOT polymer *Polymers for Advanced Technologies* 2017 DOI: 10.1002/pat.4116

Fabrication of Graphene/n-Silicon Schottky Heterojunction for Detection of Free Chlorine in Aqueous Solutions

Shayan Angizi [1], P. Ravi Selvaganapathy[2], Peter Kruse [1,*]

[1] Department of Chemistry and Chemical Biology, McMaster University, Hamilton, L8S 4M1, Canada
[2] Department of Mechanical Engineering, McMaster University, Hamilton, L8S 4M1, Canada

Abstract:
The importance of water disinfection using free chlorine, as a primary disinfectant of water, is increasing rapidly due to growing global demands for clean water. Measurement of free chlorine concentration is a crucial step to ensure its effectiveness. Herein, a novel single-layer graphene/n-silicon Schottky diode is introduced for the continuous monitoring of the free chlorine concentration in water. In this research, we investigated the exponential variation of resistance in Schottky diode design upon exposure to free chlorine, and its impact on the sensitivity of this novel platform compared with the conventional techniques. The current-voltage characteristics of the Schottky diode reveal the 3-5 times higher sensor response at free chlorine concentrations compared to conventional chemiresistors. Moreover, the output characteristic of the device shows the variation of Schottky barrier height can be up to 0.3 eV upon exposure to the globally acceptable range of free chlorine. We showed that variation of water quality parameters such as pH affects the sensing performance through modulating surface chemical/physical reactions. The calculated limit of detections for Schottky diode shows a significantly lower value compared to chemiresitive platforms so that they can be utilized as highly sensitive sensing platforms. These results can demonstrate the excellence of this novel platform for future water quality sensors.

Keywords: Graphene, Schottky diode, Schottky barrier height, surface charge transfer, free chlorine, water quality sensor.

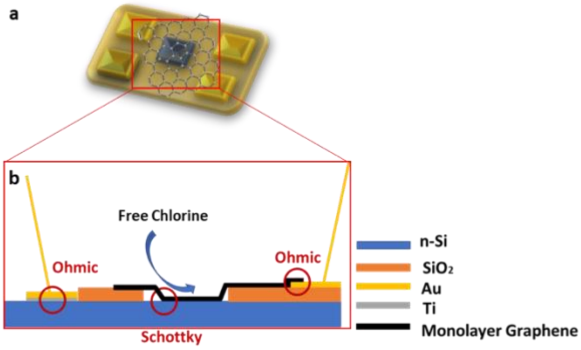


Figure 1: a) Three dimensional schematic illustration of the sensor showing both Schottky diode and chemiresistive designs, b) Cross-sectional illustration of the Schottky contact between the graphene and silicon where the graphene meets free chlorine. At the interface, Schottky barrier height is modulated due to exposure to oxidizing free chlorine through modulation of graphene’s Fermi level.

Smart Materials & Surfaces - SMS 2021 Virtual Session

Graphene liquid crystal based dielectrics

P. Poulin
Centre de Recherche Paul Pascal - CNRS Univ. of Bordeaux, 33600 Pessac, France

Abstract:

Graphene and carbon nanotubes are considered as promising fillers to make conductive polymer nanocomposites. Nevertheless, it is expected that 2D graphene, unlike 1D carbon nanotubes, display a percolation threshold altered by the formation of a liquid crystalline phase. Actually the percolation threshold of 2D graphene is expected to be greater than the percolation predicted by the classical excluded volume theory. This expectation is verified experimentally in this work. The materials are formulated by graphene oxide functionalization, and by a phase transfer method which allows the solubilization of graphene oxide monolayers in non-polar solvents. Being a bad news for making conductive composites, the greater percolation threshold of graphene materials is in fact an opportunity to develop dielectric nanocomposites with high permittivity and low losses. Deformable structures can be made by using an elastomeric matrix.

The obtained materials display a giant electrostriction coefficient (M~10-14 m2/V2 at 0.1 Hz) coupled with good reproducibility during cycles at high deformation rates. High permittivity and efficient electromechanical coupling are useful features to perform energy storage or conversion between mechanical and electrical energy for various applications of electrostrictive polymers including sensing and energy harvesting. Examples of first devices will be shown..

Li-ion batteries: characterization using EIS

X.Ramón. Nóvoa
CINTECX-ENCOMAT group, Universidade de Vigo, Vigo, Spain

Abstract:

The increasing need for clean mobility makes battery management systems (BMS) essential tools to manage packs of identical cells that form a battery. The main task of a BMS is to manage the battery pack so that it can provide a high amount of energy maintaining overall high performance[1]. The aim is to maximize life and ensure a safe operating point. For this task complete cell monitoring is required, which includes energy management during charging and discharging, temperature control, and battery impedance parameters estimation with the aim of obtaining the different states: state of charge (SoC), state of health (SoH), and state of functionality (SoF, available charging and discharging power).

We present here an EIS-based method [2] for the identification of the battery impedance parameters that inform about the charge transfer and diffusion processes at both electrodes. The model developed reproduces adequately the experimental spectra, as shown in Fig. 1, for 0% SoC and two operation temperatures. The model developed is based on an equivalent electrical circuit that involves the electrochemical processes developing at the electrodes, the contribution of the separator, and the geometry of the container.

Keywords: Electrochemical impedance spectroscopy, EIS, Li-ion batteries, state of charge, state of health .

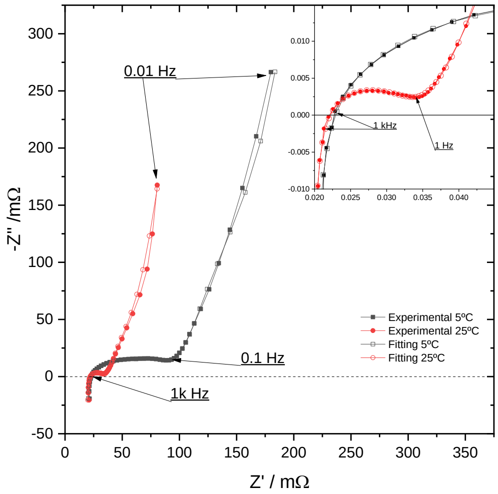


Figure 1: Experimental and fitted impedance spectra corresponding to a cylindrical cell (400 cm^2 developed surface) at 0% SoC and 5 and 25 °C..

References:

1. Fleischer, C., Waag, W., Heyn, H.M., and Sauer, D.U. (2014) On-line adaptive battery impedance parameter and state estimation considering physical principles in reduced order equivalent circuit battery models: Part 1. Requirements, critical review of methods and modeling. *J. Power Sources*, **260**, 276–291.
2. Guitián, B., Nóvoa, X.R., and Pintos, A. (2018) EIS as a Tool to Characterize Nanostructured Iron Fluoride Conversion Layers for Li-Ion Batteries. *Bulg. Chem. Commun.*, **50** (Special Issue D), 82–89.

Development of lead-free piezoelectric fibres

N. G. Azoia [1,*], A. Melo [1], B. Peliteiro [1], D Esteves [1], S. Silva [1], N. Durães [1],
[1] Centro de Nanotecnologia e Materiais Técnicos, Funcionais e Inteligentes (CeNTI), Rua Fernando Mesquita 2785, 4760-034 V. N. Famalicão, Portugal.

Abstract:

The development of new electroactive materials and their application in different structures, as fibre reinforced composites for sensing and energy harvesting, has been a common topic of research for the past decade. One of the new exploration trends is the development of advanced mono/bi-component piezoelectric (PE) fibres to be integrated into composite structures acting as piezoelectric sensors and/or harvesters. Several technologies are commonly used to develop these fibres, using mono- and bi-component extrusion and the processing of electrically active layers directly from melt spinning processes of conductor and semiconductor polymers. Developments carried out at CeNTI focused on the study of fibre processing parameters of bi-component melt-spinning technology using electroactive polymers coaxially combined with conductive polymeric compounds in the fibre cross-section will be presented. The microstructure and crystalline structure of the processed polymers was studied as a function of the processing conditions as well as its integration in composite materials. Beyond the described developments, the InComEss project proposes a new green-and-cost-effective strategy for high efficient energy harvesting by combining new smart advanced polymer-based composite materials and structures into a single/multi-source concept to harvest electrical energy from mechanical energy and/or waste heat ambient sources, which consists of three novel Energy Harvesting Systems (EHSs) configurations: Piezoelectric, Thermoelectric and hybrid Thermo/PiezoElectric EHSs. The project will demonstrate its applicability in key sectors and applications, structural health monitoring in buildings and aircraft, and monitoring vehicle, presenting the highest market potential.

Keywords: piezoelectric fibres, lead free, energy harvesting.

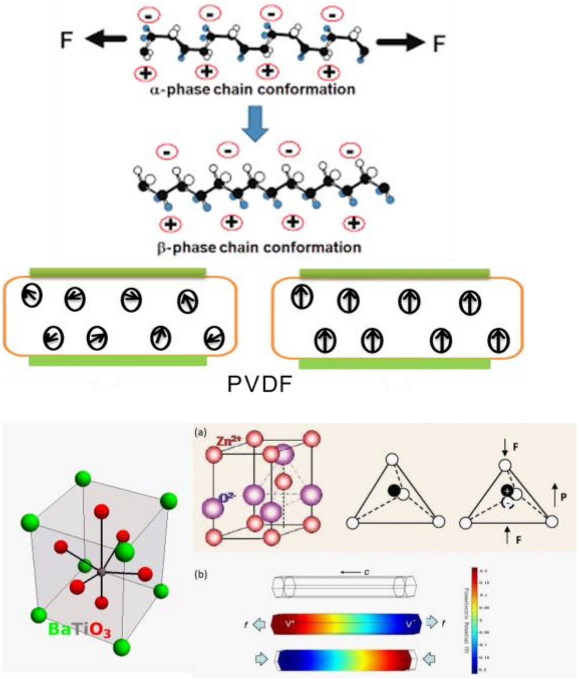


Figure 1: Lead free materials with piezoelectric properties.

Piezoelectric Vibration Energy Harvester – State of the Art Systems Implementations and Economics

J. Kunzmann and E. de Pablo Corona
Smart Materials GMBH, Germany

Abstract:

Energy harvesting systems, which use “waste” vibration energy present in the environment, have become the focus of interest during the past years. The increasing use of portable electronics, sensor-controlled systems and the growing requirement for structural health monitoring systems (SHM) for the worldwide aging building infrastructure and the new generation of composite “blackbody” aircrafts has renewed interest in designing autonomous sensor and SHM systems.

Harvesting electric energy from vibrations with piezo electric devices has been thoroughly investigated in the past and actively used in many devices for decades. Normally implemented using PZT based piezo ceramics, these devices feature a much longer life time compared with batteries but were always second choice to electromagnetic vibration harvester due to the mechanically and electronically more complicated and restricting design and higher costs. Alternative led-free piezoelectric materials are being tested at the InComEss project, which in turn might further bring the harvesting systems to an even more attractive technology.

The renewed interest in piezo electric vibration energy harvester is a combination of new market demands for structural health monitoring, the movement into renewable and sustainable energy sources, recent electronic developments for ultra-low power circuits as required for cell phones and the commercial availability of improved piezo composite materials.

At the cross section of these new materials, advanced electronics and new market demands a new generation of piezo electric vibration energy harvester has become reality, overcoming many of the restriction and draw backs of its predecesor devices.

This presentation gives an overview about the current state of the art of piezo electric vibration harvester with a special focus on the economics, efficiency, feature and benefits in comparison with other competitive technologies available

Molecular Switches at Interfaces and in Junctions: A Theoretical Insight

J. Cornil
University of Mons, Belgium

Abstract:

Interfaces play a major role in all organic-based devices by controlling the efficiency of many key electronic processes such as charge injection, exciton dissociation or charge recombination. For charge injection, there is a need to minimize the injection barriers to operate the devices at low voltages. An elegant solution is to cover the electrodes with self-assembled monolayers in order to modulate the work function of the metallic contact, and hence the energy barriers for injection. However, this approach only introduces static effects which could be supplemented by a dynamic dimension if the architecture of the SAM could be modified by an external stimulus. One strategy would be to incorporate photochromic molecules or chemical switches in the SAM in order to gain a dynamical control of the charge injection process. In the first part of the presentation, I will provide an overview of some recent theoretical efforts in this direction accomplished in close collaboration with various experimental partners [1-5].

On the other hand, the field of molecular electronics aiming at fabricating devices at the molecular scale by inserting molecules between metallic electrodes also heavily relies on interfaces. One challenge here is to design molecules able to provide a functionality to the device, such as a rectification or a switching behavior by inserting molecules addressable by external stimuli. In the second part of the presentation, I will review some recent theoretical works illustrating how the current flowing across the junction can be tuned when inserting photochromic molecules or molecular switches in junctions [6-8].

I will further illustrate that chemical design can be hampered by Fermi level pinning effects making the energy level alignment in the junction insensitive to molecular derivatization achieved on the isolated molecules [7,9].

References:

1. N. Crivillers et al., Adv. Mater. 25, 432, 2013
2. Q. Wang et al., Adv. Funct. Mat. 28, 1800716, 2018
3. V. Diez-Cabanes, Adv. Mater. Technol. 3, 1800152, 2018
4. A. Galanti et al., J. Am. Chem. Soc. 140, 16062, 2018 ; V.
5. Diez-Cabanes et al., ACS. Appl. Mat. Int. 13, 27737, 2021
6. S. Osella et al., J. Phys. Chem. C 118, 18721, 2014
7. C. Van Dyck et al., 24, 6154, 2014
8. M. Souto et al., Phys. Chem. Chem. Phys. 20, 25638, 2018
9. S. Rodriguez-Gonzalez et al., 9, 2394, 2018.

MICATRONICS: A NEW PLATFORM FOR SOFT TRANSPARENT TECHNOLOGY

Ying-Hao Chu
Department of Materials Science & Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan

Abstract

A new world is being formed based on the technologies composed of artificial intelligence, Internet of Things (IoT), and robots. Especially, in the research fields of IoT and robotics systems, a device with mechanical flexibility can deliver more degrees of freedom as far as the design aspects are concerned. Therefore, the development of soft and flexible electronics becomes an important research direction for wearable and IoT devices. Due to the mechanical flexibility, polymer materials and thin metal foils are commonly used in the fabrication of flexible electronic systems. However, the reliability issue under practical operations hinders the applications of these flexible electronics, especially for those on polymer based substrates. This is attributed to a mismatch of thermal expansion coefficient between substrate and functional materials or low thermal and chemical endurance of polymers and organic materials. A lot of researchers are working hard and together to expand the applicability of current flexible devices. However, new pathway to flexible electronics can also be developed in parallel to provide more subtle solutions, thus in need of new platform to integrate functional materials with good thermal and chemical stabilities together with mechanical flexibility. In this research field, oxides can play an important role due to their intriguing functionalities and superior thermal and chemical stabilities. To deliver high-quality thin films or structures based on oxides, heteroepitaxy is essential. However, the lack of a suitable approach remains an obstacle for flexible oxide heteroepitaxy. van der Waals epitaxy (vdWE) involving two-dimensional layered materials can play a crucial role in the expansion of thin film epitaxy by overcoming the bottleneck of material combinations due to lattice/thermal matching conditions inherent to conventional epitaxy. In this study, we use a 2D material as the substrate. In this talk, we confine ourselves to the validity of vdWE of functional oxides on muscovite mica throughout this treatise. With such demonstrations, it is anticipated that MICAtronics, vdWE on mica, can reveal unusual properties and emergent phenomena in the realm of high-performance flexible device applications.

Laser based pick and place of 2D nanomaterials

N.T. Goodfriend[1*], O. Gatsa[1], A.V. Bulgakov[1], O. A. Nerushev[2], T. Hotta[3], C. Zhao[3], R. Kitaura[3], E.E.B. Campbell[2], N.M. Bulgakova[1], Tomas Mocek[1]

1- HiLASE Centre, Institute of Physics of the Czech Academy of Sciences, Za Radnici 828, 25241 Dolní Břežany, Czechia
2- EastCHEM, School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, United Kingom
3- Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan

Abstract:
Two dimensional nanomaterials are a key material for development of nanodevices such as sensors, diodes, transistors, aswell as quantum and opto-electronics. This is due to the wide array of material options coincident with variable bandgaps and absorption curves. This enables nanoconductors, insulators and semiconductors such as graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMD) respectively. However, these properties are difficult to preserve during the current processes of generation and assembly of devices. We present a novel method of 2D material positioning based upon the technique of laser induced forward transfer.

Laser induced forward transfer (LIFT) is amethod of back irradiation of a material which provides the impulse for transfer from a position on a donor substrate to a chosen location on a receiver. This presentation aims to demonstrate how the utilization of a metal dynamic release layer which absorbs the irradiation pulse resulting in a blisterlike deformation which mechanically removes the surface material and transfers this to a new location on a receiver substrate. This method otherwise known as blister based LIFT has been shown to transfer single layer TMDs and preserve the initial properties of the initial film before and after transfer by Goodfriend et al.[1,2] The work presents advances of these studies and demonstrates the method as compatible for nano-insulators such as hBN and conductors such as graphene. Furthermore, the effect of the seperaration distance between the donor and receiver film was investigated whilst the laser pulse duration was also varied from fs to ns pulse. The development of this technique shows promise for generation of stacked 2D heterostructures alongside precise and rapid positioning of these structures.

Keywords: two dimensional nanomaterial, blister based laser induced forward transfer, ultrashort laser pulses, micropatterning, 2D heterostructure applications, nanotechnology.

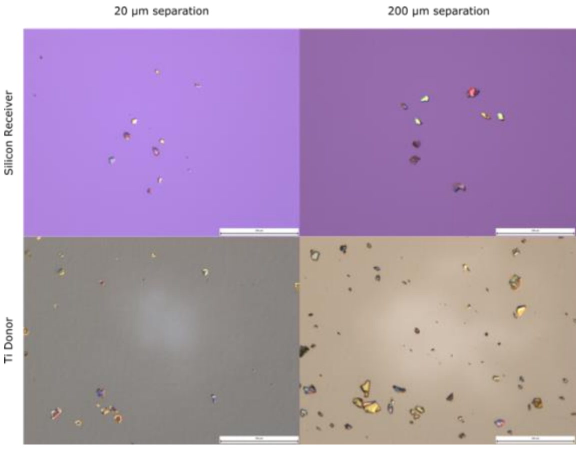


Figure 1: Optical image of the transfer of exfoliated hBN from a donor film via nanosecond pulse duration BB LIFT at both near and far separation of donor film and receiver substrate.

References:

1. N. T. Goodfriend, S. Y. Heng, O. A. Nerushev, A. V. Gromov, A. V. Bulgakov, M. Okada, R. Kitaura, J. H. Warner, H. Shinohara, W. Xu, E. E. B. Campbell, (2018) Blister-based-laser-induced-forward-transfer: A non-contact, dry laser-based transfer method for nanomaterials, *Nanotechnology* 29, 385301.
2. A. V. Bulgakov, N. T. Goodfriend, O. Nerushev, N. M. Bulgakova, S. V. Starinskiy, Y. G. Shukhov, E. E. B. Campbell, (2014) Laser-induced transfer of nanoparticles for gas-phase analysis, J. Opt. Soc. Am. B, 31, C15.

Extending the scope for Curcuminoids: from active components on graphene devices to the creation of 2D materials

N. Aliaga-Alcalde [1,2,*], A. González-Campo [2], D. Herrera-Miranda[2], R. Zaffino[2], D. Riba-López[2], T. Carcona-Lamarca[2], R. Díaz-Torres[2], L. Rodríguez-Cid[2], C. Domingo[2], Mònica Soler[3], Herre van der Zant[4], Eliseo Ruiz[5]

[1] ICREA (Institució Catalana de Recerca i Estudis Avançats), Passeig Lluís Companys, 23 08018 Barcelona, Spain

[2] ICMAB-CSIC (Institut de Ciència dels Materials de Barcelona), Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

[3]Departamento de Ciencia de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile

[4]Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

[5]Universitat de Barcelona, Facultat de Química, Diagonal 645, 08028 Barcelona, Spain

Abstract:

Curcuminoids (CCMoids) are organic molecules well-known because of their biological and medical applications.[1] Lately, these conjugated organic systems have triggered the interest of researchers from additional fields, introducing CCMoids as active layer components in organic sollar cells, bioMOFs, single-molecule magnets, small ions sensors, logic gate elements and as liquid crystals, among others.[2]

In this respect, our group specializes in the synthesis and characterization of CCMoids toward their integration on different substrates and nanodevices.[3] This synopsis emphasizes our work in the creation of three-terminal devices based on few-layers graphene, where our CCMoids function as nanowires and the final setups perform at room temperature, together with the evolution of our work in this subject.[4-5]

In addition, the proper design of CCMoids allows the creation of organic and coordination polymers (OPs and CPs). Among them, it is stress a family of 2D materials containing a suitable CCMoid coordinated to Zn(II) and Co(II) ions, respectively.[6-7]

Our purpose here is to highlight the versatile chemistry and potential of CCMoids focusing on the areas of molecular electronics and sensors.

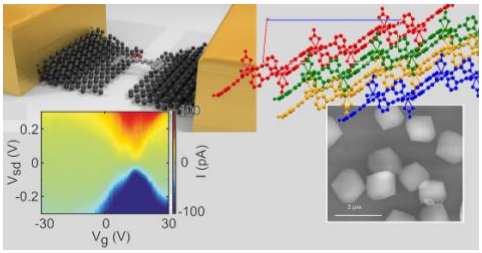


Figure 1: Figure illustrating (left) a three terminal nanodevice based on few-layer graphene and (right) 2D coordination polymer, both containing CCMoids.

Keywords: curcumin derivatives, curcuminoid, 2D coordination polymer, graphene, three-terminal device, electronic transport studies

References:

1. Tomeh, M. A.; Hadianamrei, R.; and Zhao X. (2019) A review of curcumin and its derivatives as anticancer agents, *Int. J. Mol. Sci.*, 20, 1033 (1-26pp).
2. Díaz-Torres R. *et al.* (2016), Multiscale study of mononuclear CoII SMMs based on curcuminoid ligands, *Chem. Sci.*, 7, 2793-2803.
3. I. J. Olavarría-Contreras *et al.* (2018) Electric-field induced bistability in single-molecule conductance measurements for boron coordinated curcuminoid compounds, *Chem. Sci.*, 9, 6988-6996.
4. F. Prins *et al.* (2011) Room-temperature gating of molecular Junctions using few-layer graphene nanogap electrodes, *NANO Lett.*, 11, 4607-4611.
5. E. Burzurí *et al.* (2016) Sequential electron transport and vibrational excitations in an organic molecule coupled to few-layer graphene electrodes, *ACS Nano*, 10, 2521-2527.
6. L. Rodríguez-Cid *et al.* (2020) Novel Zn(II) coordination polymers based on the natural molecule bisdemethoxycurcumin, *Cryst. Growth & Des.*, 20, 6555-6564.
7. L. Rodríguez-Cid *et al.* (2021) Broadening the scope of high structural dimensionality nanomaterials using pyridine-based curcuminoids, *Dalton Trans.*,50, 7056-7064.

Curcuminoid-based active surfaces towards the development of new metal heterogeneous detectors

A. González-Campo,*[1] R. Gimeno-Múñoz,[1] N. Aliaga-Alcalde,[1,2]
[1]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la Universitat
Autònoma de Barcelona, 08193 Bellaterra, Spain. [2]ICREA (Institució Catalana de Recerca i Estudis
Avançats), Passeig Lluís Companys, 23, 08018 Barcelona, Spain. email: agonzalez@icmab.es

Abstract:

The development of new metal detection devices is a subject of growing interest in the scientific community. Many heavy metals are found in chemical or biological species that collaborate in essential processes, and control of their presence and amount is crucial. Their monitoring is necessary to provide insight in their toxicity, their effects on the environment, the development of diseases due to the excess or deficiency of these metals and/or the study of new drugs based on inorganic chemistry. Regarding this matter, the design of fluorophores, for metal fluorometric detection, that can be switched on or off or exhibit a shift in their emission upon reaction with the analyte is a straightforward approach highly desired. Advances in molecular design have involved the preparation of multifunctional molecular materials, including the synthesis of bifunctional probes or heterogeneous sensors [1]. Here, knowing the great chemical versatility of Curcuminoids (CCMoids), new fluorescent CCMoids and their immobilization on surfaces has been explored. CCMoids are derivatives of curcumin exhibiting conjugated features, and fluorescent behaviour with the possibility of coordinating both metals and metalloids, affecting this the electronic/fluorescent performance.[2] Therefore, the shifts in the fluorescence of the surfaces, depending on the metal or metalloid coordinated, together with the possibility of the metal released upon coordination have been analyzed, obtaining an increase, decrease or even a switch of the surface fluorescence depending on the metal/metalloid under study, Figure 1.

Keywords: curcuminoids, fluorescence, surface chemistry, sensor, detector, metals, responsive surface.

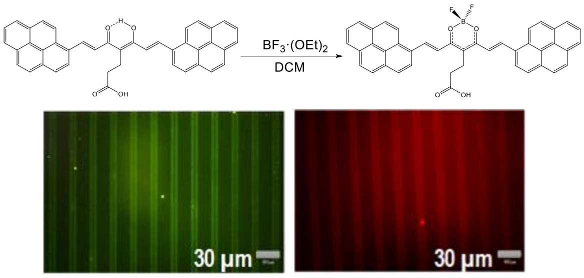


Figure 1: On-site coordination of β-diketone with BF3 complex in dichlorometane (DCM). The BF2 group modifies the fluorescent properties of the system, losing emission in the green region and emitting with greater intensity in the red, near the IR.

Acknowledgements This work was supported by the projects PID2019-108794GB-100 (AEI/FEDER, UE), SGR (1277) and ERC 724981 (Tmol4Trans). AGC thanks for the Ramon y Cajal Grant (RYC-2017-22910)

References:

1. Pei-Pei, J.; Shu-Ting, J.; Lin, X. (2019), Small-molecule Bifunctional Fluorescent Probes for the Differential Detection of Multiple Guests, *Curr. Org. Synth.*, 16, 485.
2. a) Burzurí, E.; Island, J. O.; Diaz-Torres, R.; Fursina, A.; González-Campo, A.; Roubeau, O.; Teat, S. J.; Aliaga-Alcalde, N.; Ruiz, E.; van der Zant, H. S. J. (2016), Sequential electron transport and vibrational excitations in an organic molecule coupled to few-layer graphene electrodes, *ACS Nano*, 10, 2521. b) Díaz-Torres, R.; Menelaou, M.; Roubeau, O.; Sorrenti, A.; Brandariz-De-Pedro, G.; Sañudo, E.C.; Teat, S.J.; Fraxedas, J.; Ruiz, E.; Aliaga-Alcalde, N. (2016), Multiscale study of mononuclear CoII SMMs based on curcuminoid ligands, *Chem. Sci.*, 7, 2793.

Smart Electromagnetic Surfaces: A Key-Enabling Technology for Future Wireless Systems

M. Barbuto [2], Z. Hamzavi-Zarghani [2], M. Longhi [1], A. Monti [1], D. Ramaccia [2], S. Vellucci [2,], A. Toscano [2], F. Bilotti [2,*]
[1] Department of Engineering, Niccolò Cusano University, 00166, Rome, Italy.
[2] Department of Industrial, Electronic, and Mechanical Engineering, ROMA TRE University, 00146, Rome, Italy

Abstract:

When switching from 5G to beyond 5G wireless systems, the key-performance-indicators (KPIs) dramatically change, introducing unprecedented challenges in terms of massive capacity, almost-zero latency and jitter, ultra-high reliability, and security.

In order to take such challenges, the spectrum to host future wireless systems will use ever higher frequencies, characterized by a mm-scale wavelength, introducing, thus, a number of issues in the electromagnetic propagation, due to the fast free-space attenuation and to the undesired effects caused by the obstacles in the environment.

In addition, in order to comply with the new KPIs, the use of current wireless technologies, even the most advanced ones, seems to be inappropriate. The number of access-points and base stations, in fact, would be too large to be handled and the massive local computation required by the extreme hardware virtualization of 5G systems prevents fulfilling latency and jitter requirements needed to achieve seamless connectivity for everybody and everything.

The result is that a paradigm change in the key-enabling technology is needed if we want to meet the KPIs required by future wireless systems, which are not only focused on communications but will also integrate a number of functionalities, such as sensing, data extraction and processing, localization, smartness, position awareness, etc.

In this framework, the role that electromagnetic engineering will play in the future is expected to be very relevant. In fact, in order to reduce the massive local computation, which makes current massive MIMO systems unsuitable for beyond-5G wireless systems, we need reducing hardware virtualization to a minimum. In other words, most of the functionalities that during the years have been transferred from the physical layer to the signal processing and protocol levels, must be handled back by the physical layer, allowing the processing of the signals at the speed of light.

All of this, is made possible by the significant advancements made in the last two decades in applied electromagnetics and, in particular, in smart electromagnetic materials and surfaces. Thanks to the concepts of metamaterials and metasurfaces, in fact, we are able today to design and fabricate engineered artificial materials with ad hoc properties, resulting from an unprecedented interaction with the electromagnetic field. Metamaterials and metasurfaces are not only the support where devices are built on, but they themselves integrate a number of functions.

Metasurfaces are physically realized as a periodic/aperiodic arrangement of electrically small particles, whose separation is electrically small, as well. The possibility to control/reconfigure/program the electromagnetic response of the individual particles constituting the metasurface through different physical mechanisms (e.g. electronic circuits, temperature, liquid crystals, light, etc.) enables a huge number of degrees of freedom in terms of operation and functionalities.

In particular, such smart surfaces can be used to cover the external surfaces of the objects present in the indoor/outdoor environment so that the objects themselves do not behave as mere obstacles for the mm-wave but, rather, have an active role in establishing and keeping line-of-sight links. Smart electromagnetic surfaces can be also used to enable cognitive features, position awareness, routing and forwarding, etc.

Some concrete examples of how smart electromagnetic surfaces can contribute to the development of future wireless systems will be given at the conference through the presentation of the recent research results obtained by our group [1].

Keywords: smart electromagnetic surfaces, metamaterials, metasurface, future wireless systems.

References:

1. Barbuto, M., Marini, A.V., Monti, A., Ramaccia, D., Vellucci, S., Toscano, A.,

Bilotti, F., (2020) Metasurfaces 3.0: a Key Enabling Technology for the Development of beyond-5G Communication Systems, *Metamaterials 2020*, doi: 10.1109/Metamaterials49557.2020.9285131

Emerging Applications of Boron Nitride Nanotubes for Advanced Electronics and Biomedicine

Yoke Khin Yap
Department of Physics, Michigan Technological University, Houghton, Michigan 49931, United States
Elizabeth and Richard Henes Center for Quantum Phenomena, Michigan Technological University, Houghton, Michigan 49931, United States

Abstract:
The electrically insulating and optically transparent boron nitride nanotubes (BNNTs) have found novel applications in advanced electronics and bio-imaging. Although these physical properties are not favorable for conventional electronics and energy applications, recent advancement in controlled synthesis of BNNTs has enabled the demonstration of a series of unique applications.[1-3] For example, We demonstrated that BNNTs are unique one-dimensional templates for room-temperature single-electron transistors (SETs)[4], and two-dimensional gold quantum dots with tunable optical bandgap[5]. We also reported field-effect transistors (FETs) by van der Waals Tellurium (Te) atomic chains[6]. We have also demonstrated immunophenotyping of antigens by flow cytometry.[7] Some of the emerging applications summarized in Figure 1 [8] will be discussed in the meeting.

Keywords: Boron nitride nanotubes, single-electron transistors, atomic chains, fluorescence spectroscopy, flow cytometry.

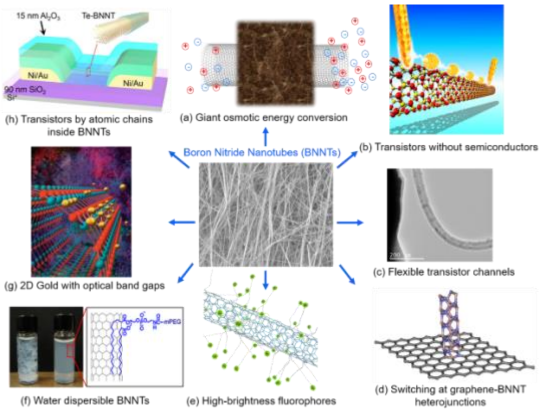


Figure 1: Graphical representations of some emerging applications of BNNTs.[8] (a) Osmotic power harvesting, (b) transistors without semiconductors, (c) flexible transistor channels, (d) graphene-BNNT heterojunctions, (e) high-brightness fluorophores, (f) water dispersible BNNTs, (g) 2D gold on BNNTs, (h) transistor by atomic chains inside BNNTs. Copyright 2021 American Chemical Society.

References:

1. Lee, C. H., Xie, M., Kayastha, V., Wang, J., Yap, Y. K. (2010) Patterned growth of boron nitride nanotubes by catalytic chemical vapor deposition, *Chem. Mater*. 22, 1782-1787.
2. (Review) Wang, J., Lee, C. H., Yap, Y. K. (2010) Recent advancements in boron nitride nanotubes, *Nanoscale* 2, 2028-2034.
3. (Review) Lee, C. H., Bhandari, S., Tiwari, B., Yapici, N., Zhang, D., Yap, Y. K. (2016) Boron nitride nanotubes: recent advances in their synthesis, functionalization, and applications, *Molecules* 21, 922.
4. Lee, C. H., Qin, S., Savaikar, M. A., Wang, J., Hao, B., Zhang, D., Banyai, D., Jaszczak, J. A., Clark, K. W., Idrobo, J-C., Li, A-P., Yap, Y. K. (2013) Room-temperature tunneling behavior of boron nitride nanotubes functionalized with gold quantum dots, *Adv. Mater.* 25, 4544-4548.
5. Bhandari, S., Hao, B., Waters, K., Lee, C. H., Idrobo, J-C., Zhang, D., Pandey, R., Yap, Y. K. (2019) Two-dimensional gold quantum dots with tunable bandgaps, *ACS Nano* 13, 4347-4353.
6. Qin, J-K., Liao, P-Y., Si, M., Gao, S., Qiu, G., Jian, J., Wang, Q., Zhang, S-Q, Huang, S., Charnas, A., Wang, Y., Kim, M. J., Wu, W., Xu, X., Wang, H-Y., Yang, L., Yap, Y. K., Ye, P. D. (2020) Raman response and transport properties of tellurium atomic chains encapsulated in nanotubes, *Nature Electronics* 3, 141-147.
7. Yap, Y. K., Zhang, D., Yapici, N. (2017) High-brightness Fluorophores, *US Patent Application* US20180296705A1.
8. (Review) Zhang, D., Zhang, S-Q., Yapici, N., Oakley, R., Sharma, S., Parashar, V., Yap, Y. K. (2021) Emerging applications of boron ntride nanotubes in energy harvesting,

electronics, and biomedicine, *ACS Omega* 6, 20722-20728.

Rational Design of $Rb^{I}_{x}Mn^{II}[Fe^{III}(CN)_6]_{(2+x)/3}.zH_2O$ (RbMnFe) Prussian Blue Analogue (PBA) Nanoparticles (NPs) for Switchable Magnetic and Non-linear Optical Properties

T. T. Vu[1], N. Daro[1], S. Mornet[1], E. Freysz[2], G. Chastanet[1]

[1] ICMCB, University of Bordeaux, 87 avenue du Dr Albert Schweitzer, 33600 Pessac, France
[2] LOMA, University of Bordeaux, 351 Cours de la Libération, 33400 Talence, France

Abstract:

Rubidium Manganese hexacyanoferrate, $Rb^{I}_{x}Mn^{II}[Fe^{III}(CN)_6]_{(2+x)/3}.zH_2O$ (RbMnFe), one of the Prussian blue analogues, is an interesting material with multifunctional properties (ferromagnetic, ferro-electric, photo-switchable…) arising from the electron transfer between the Mn^{II} and the Fe^{III}. This electron transfer can be triggered by external stimuli such as temperature, light, pressure, and electrical field and is associated to a change in the properties with memory effect around room temperature over 100 K range. At low temperature, the Mn^{III} ion exhibits a Jahn-Teller distortion giving rise to the change in the symmetry from cubic high temperature phase (F-43m) to tetragonal low temperature phase (I-4m2). Both phases are non-centrosymmetric leading to second harmonic generation. Therefore, we can follow the electronic transition by probing the change in the magnetic susceptibility, in the second order non-linear susceptibility, in the structure and in the vibrations of the compound. These changes of properties depend on the amount of Rb^+ inserted in the 3D structure: below 60% of Rb content, the electron transfer is suppressed and the compound becomes centrosymmetric. The RbMnFe properties have been studied extensively in the micro-scale, however there is a huge lack of investigation of this compound at the nanoscale of importance for further integration in multifunctional devices.

In this study, we report the rational design of switchable RbMnFe nanoparticles. This required to combine both the size reduction of the compound to the nanoscale and to preserve high Rb content to observe the switching properties. We also shed the light on how to have access to the composition of the compound with high accuracy using two different reliable techniques (inductively coupled plasma and X-ray diffraction refinement). Furthermore, we illustrate not only the size reduction effect on the magnetic and non-linear optical properties, but also the composition impact on these properties.

Keywords: Prussian blue analogue, nanoparticles, switching properties, non-linear optical properties.

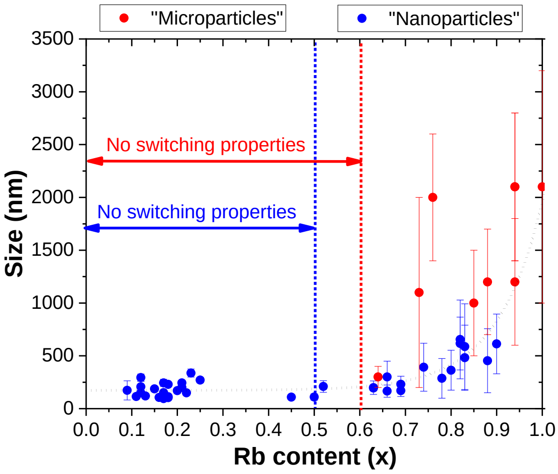


Figure 1: The evolution of the size *vs.* Rb content (x) for “microparticles” (in red) and “nanoparticles” (in blue).

References:

1. Ohkoshi, S., Matsuda, T., Tokoro, H., Hashimoto, K., (2005) A surprisingly large thermal hysteresis loop in a reversible phase transition of $Rb_xMn[Fe(CN)_6]_{(2+x)/3}.zH_2O$, *Chem. Mater.*, 17, 81 – 84.
2. Ohkoshi, S., Saito, S., Matsuda, T., Nuida, T., Tokoro, H., (2008) Continuous change of second-order nonlinear optical activity in a cyano-bridged coordination polymer, J. Phys. Chem C, 112, 13095 – 13098.

Transport of Magnetic Microparticles on a Self-Assembled 2D Lattice through an Externally Monitored Potential

F. Martínez-Pedrero[1,*], F. Ortega[1,2] R.G. Rubio[1,2] and C. Calero[3,4,5]

[1]Departamento de Química-Física, Universidad Complutense de Madrid, Spain.
[2]Inst. Pluridisciplinar, Universidad Complutense de Madrid, Spain
[3]Condensed Matter Physics Department, Faculty of Physics, Universitat de Barcelona, Spain
[4]Institut de Nanociència i Nanotecnologia, IN2UB, Universitat de Barcelona, Spain
[5]Universitat de Barcelona Institute of Complex Systems, Spain

Abstract:

The study of the collective motion of active/actuated colloids in confined environments opens a promising avenue for manipulating molecules or microcargos in the low Reynolds number regime and sheds light over transport mechanisms in biological systems. In fluid interfaces, where the state of these confined systems are deeply determined by their in-plane spatial distribution, by small variations in the particle contact angle and by specific interactions with the boundaries, the main strategies for transporting colloids are based on surface waves, magnetocapillary and Marangoni effects, or self-generated gradients.

In this work, we show that magnetic microspheres asymmetrically adsorbed at a flat fluid interface can be transferred between different-sized spheres equally confined. The magnetic colloidal suspension, energized by a precessing and flashing magnetic field, serves as a dynamic lattice in which smaller magnetic spheres are collectively transported on planned two-dimensional trajectories. By changing the strength, frequencies, and tilt angle of the flashing/precessing field, the driven microspheres display random or deterministic motion. The gradual increase in the number of motile entities leads to an inverted scenario where the particles that formed the lattice before are conveyed on a monolayer of the initially motile ones. The studied system, easy to implement and monitor, can be used in the transport of molecules or colloidal cargos on flat fluid interfaces.

Keywords: dynamic self-assembly, 2D confined systems, superparamagnetic particles, fluid interface, colloidal transport

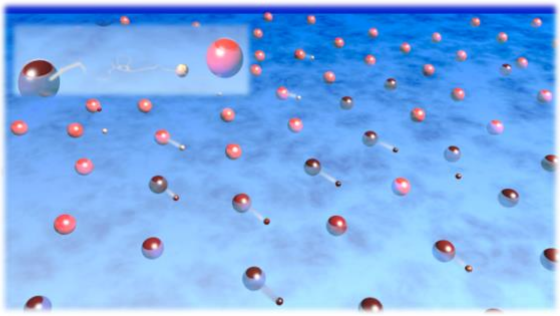


Figure 1: The sheme represent an easily implementable strategy wherein small microparticles adsorbed at a fluid interface are transported through a lattice of larger spheres, in a practically deterministic motion, by periodically inverting the vertical component of a precessing field.

References:

1. G. Grosjean, M. Hubert, Y. Collard, S. Pillitteri, N. Vandewalle. *Eur. Phys. J. E*, 2018, 41, 137.
2. F. Martínez-Pedrero, F. Ortega, J. Codina, C. Calero, R. G. Rubio. *J. Colloid Interface Sci.*, 2020, 560, 388.
3. F. Martínez-Pedrero, F. Ortega, R. G. Rubio, C. Calero. *Advanced Functional Materials*, 2020, 2002206, DOI: 10.1002/adfm.202002206.

Challenges on fabrication of the microstructured magnetic actuation systems based on Ni-Mn-Ga single crystal

D. Musiienko[1], M. Kohl[2], O. Heczko[1]

[1] Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic
[2] Institute of Microstructure Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany

Abstract: Ni-Mn-Ga off-stoichiometric magnetic shape memory (MSM) alloys are known for their large reversible magnetic-field-induced strain (MFIS) of several percent accompanied by significant change in magnetic properties [1]. The mechanism behind the MSM effect is the magnetically induced reorientation (MIR) of the crystal lattice in martensite phase. Martensitic twin variants with the short crystallographic c-axis (axis of easy magnetisation) oriented along the applied magnetic field grow at the expense of other variants with different orientation. A significant advancement in the MSM applications development would be the actuation at micro- and nanoscale: the decrease of the MSM element size should lead to the proportional mass reduction, allowing for significant increase of the operating frequency.

We report on the fabrication and properties of the prototypes of micro-magneto-mechanical systems (M³S) by using top-down approach, i. e. decreasing the dimensions of a bulk Ni-Mn-Ga single crystal with defined composition and known properties. Prototyping technologies (FIB milling, electro-chemical etching and wet etching) for MSM microdevices were developed and used for fabrication of the micropillars. The representative SEM image of FIB milled micropillar is shown in Fig. 1.

We observed a sharp difference in dynamics of type I and type II twin boundaries at the microscale [2]. The measured actuation velocities of 0.18 and 1.3 (m/s) for type I and type II TBs correspond well to the previously reported values for bulk, mm-sized samples [3]. The actuation acceleration of micropillars was found to be approximately an order of magnitude larger than in bulk samples, demonstrating a well-pronounced scaling effect connected to the decrease of cross-section in actuated MSM crystals and therefore the reduction of moving mass. Twinning stresses for single twin boundaries motion in micropillars were revealed to be ~2.3 MPa for type I twins and ~0.8 MPa for type II [2]. It is suggested that increased twinning stress values (in comparison to the values for bulk material) are related to the incomplete removal of surface defects. It was demonstrated that in studied Ni-Mn-Ga single crystalline micropillars giant MFIS of more than 6 % can be obtained in about 5 μs [2].

Presented results suggest the possibility of fabricating Ni-Mn-Ga based M³S with bandwidth of 105 Hz, which is an order higher than previously reported [4]. Similarly, to microelectromechanical systems (MEMS) the idea behind the M³S is to provide new building blocks for the engineers in development of modern sustainable and energy efficient devices.

Keywords: Ni-Mn-Ga, magnetic shape memory, microfabrication, actuation.

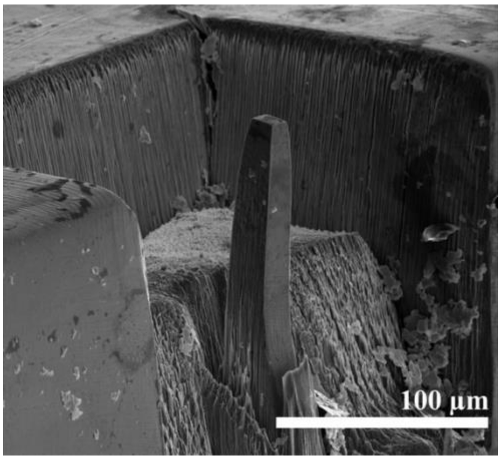


Figure 1: SEM image of the Ni-Mn-Ga micropillar.

References:

1. I. Aaltio et al. “Giant Magnetostrictive Materials”. In: *Reference Module in Materials Science and Materials Engineering* (2016), p. 14.
2. D. Musiienko et al. “Ultrafast actuation of Ni-Mn-Ga micropillars by pulsed magnetic field”. In: *Scripta Materialia* 162 (2019), pp. 482–485.
3. A. Saren et al. “Pulsed magnetic field-induced single twin boundary motion in Ni–Mn–Ga 5M martensite: a laser vibrometry characterization”. In: *Scripta Materialia* 113 (2016), pp. 154–157.
4. E. Faran, and D. Shilo. “Ferromagnetic Shape Memory Alloys – Challenges, Applications, and Experimental Characterization”. In: *Experimental Techniques* 40, pp. 1005–1031.

Biomimetic fiber webs based on conducting polymer with actuation and self-sensing capabilities

M. Beregoi [1*], A. Evanghelidis[1], I. Enculescu [1]
[1] Multifunctional Materials and Structures Laboratory, National Institute of Materials Physics, Magurele-Ilfov, Romania

Abstract:

Development of cheap biomimetic devices with aspects and functionalities similar with natural models represent an importat step in progess of human quality of life improvement. As well, the precursor material miniaturization leads to more complex devices with unexptacted features. Electrospinning is such a technique which allows the preparation of soft, light, low dimension, fibrillary webs with applications in various domains, a very interesting and challenging field being soft robotics (especially soft robots for biomedical devices). Artificial muscles belong to soft robotics field and are devices that can transform any kind of energy in mechanical motion. But if such device with superior actuation properties generates a movement and in the same time feels changes of an external stimulus, getting closer to natural muscle model features? Maybe, this means that a step ahead in biomimetics was performed. In the context of dual artificial muscle/sensor fabrication, a lot of precursor materials like dielectric elastomers[1], gels[2], carbon nanotubes[3], piezoelectric structures[4] and conducting polymers[5] were tested. However, the last class is still attracting researchers attention due to low operation voltages, fast response time, high actuation performances and synthesis versatility.

In order to get even closer to natural muscle, electrospun fiber webs coated with a conducting polymer were prepared and their actuation and sensing abilities were demonstrated. Thus, fiber networks of nylon 6,6 (Fig. 1c) were prepared by electrospinning a polymer solution in preset experimental parameters that were chosen is such a way as to obtain nets with favorable densities and morphologies. Further, the freestanding fiber webs attached on copper frames were sputter covered with a thin gold layer in order to make them conductive. In the end, the metalized fibers were transferred onto stainless stell frames for driving the electrochemical deposition of the conducting polymer (polypyrrole). For testing their sensing (Fig. 1(a,b)) and actuation performances, strips from the electroactive material were taken and analyzed. As well, a morphological, structural and electrochemical characterization was performed.

Keywords: polyrrole, conducting polymers, artificial muscles, electrospinning, sensors, fibers, electrospun webs, biomimetic devices, electroactive materials, dual devices.

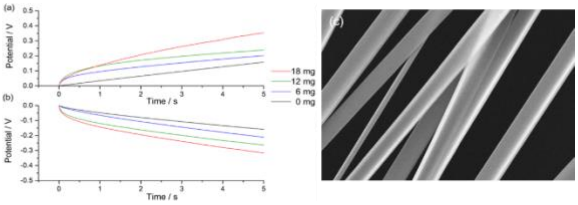


Figure 1: (a,b) Potential versus time as function of weight registered by applying +5 µA (a) and -5 Ma, respectively; (a) SEM image of the obtained electrospun fiber;

References:

1. J.-H. Bae, S.-H. Chang. PVDF - based ferroelectric polymers and dielectric elastomers for sensor and actuator applications: a review, Funct. Compos. Struct. 1 (2019) 012003.
2. K. Uh, B. Yoon, C.W. Lee, J.-M. Kim. An Electrolyte-Free Conducting Polymer Actuator that Displays Electrothermal Bending and Flapping Wing Motions under a Magnetic Field, ACS Appl. Mater. Interfaces 8 (2016) 1289–1296.
3. Y. Xiao, J. Lin, J. Xiao, M. Weng, W. Zhang, Peidi Zhou, Z. Luo, L. Chen. A multi-functional light-driven actuator with an integrated temperature-sensing function based on a carbon nanotube composite, Nanoscale 13 (2021) 6259-6265.
4. L.S. Fang, C.Y. Tsai, M.H. Xu, S.W. Wu, W.C. Lo, Y.H. Lu, Y.K. Fuh. Hybrid nano-textured nanogenerator and self-powered sensor for on-skin triggered biomechanical motions, Nanotechnology 31 (2020) 155502.
5. M. Beregoi, A. Evanghelidis, V. Diculescu, H. Iovu, I. Enculescu. Polypyrrole actuator based on electrospun microribbons, ACS Appl. Mater. Interfaces 9 (2017) 38068-38075.

Shaped organic printed films for photosensing devices

S. Sequeira [1,2,3,*], V. C. Martins [1], R. Vilarinho [4], J. Agostinho Moreira [4], S. Cardoso [1,2], H. Alves [3], D. C. Leitao [1,2]

[a] Instituto de Engenharia de Sistemas e Computadores – Microsistemas e Nanotecnologias (INESC MN), Rua Alves Redol 9, 1000-029 Lisboa, Portugal
[b] Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1000-029 Lisboa, Portugal
[c] CICECO, Universidade de Aveiro, Campus de Santiago, 3810-183 Aveiro, Portugal
[d] IFIMUP and Physics and Astronomy Department. Faculty of Sciences of University of Porto. Rua do Campo Alegre s/n. 4169-007 Porto, Portugal

Abstract:

The pursuit for alternatives to inorganic materials such as silicon as led to the uprising of organic single-crystalline materials. As a result, their long-range order, few grain boundaries, minimal defects, long diffusion length, high charge carrier mobilities and high responsivity in the visible range these materials are being vastly applied in the optoelectronic field (e.g. transistors, solar cells, light emitting diodes).

The challenge is to provide reproducible and high optoelectronic performance without compromising the feasibility and scalability of the processing method [3]. As well as, comprise proper molecular packing and precise patterning into-well defined geometric features. Thus, a strategy was developed to selectivelly grow customize printed films from a dispensed organic solution. Herein, non-contact printing was combined with surface energy engineering to locally modify the surface wettability and confine the organic solution to assigned locations, as shown in Figure 1. Therefore, films with different geometries (e.g. rectangular, circular and quandrangular) down to the microscale can be obtained. The structural properties of the printed films were studied using microRaman spectroscopy to confirm the lack of impurities and infer about their crystallinity.

To validate the applicability of this approach, a solution of TIPS-pentacene (10 mg/mL in toluene) was dispensed on wettability patterned substrates with microfabricated photosensing devices, namely photoconductors (two-terminal device) and phototransistors (three-terminal device). The optoelectronic characterization included current-voltage (IV) and time-depent current I(t) curves and output and transfer characteristics under dark and under white light illumination for photoconductors and phototransistors, respectively. Strategies to improve the present results will be further discussed.

Keywords: surface energy engineering, solution confinement, wettability assisted process, micropatterned photoactive organic materials, non-contact printing, photosensing devices.

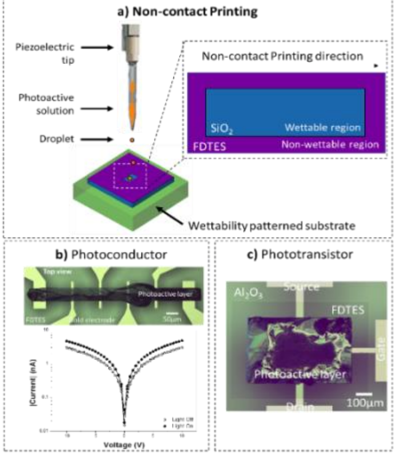


Figure 1: a) Schematic of the wettability assisted non-contact printing process to obtain micropatterned photoactive organic films and their integration into photosensing devices: b) photoconductors and c) phototransistors.

Acknowledgments: FCT for funding CICECO (UIDB/50011/2020 & UIDP/50011/2020), UID/05367/2020, PTDC/CTM-NAN/4737/2014, and NORTE-01-0145-FEDER-22090. D. C. Leitao and S. Sequeira acknowledge financial support through FSE/POPH and doctoral scholarship SFRH/BD/129827/2017, respectively.

References:

1. Jiang, H. et al. (2020), The Emergence of Organic Single-Crystal Electronics, *Angew. Chem. Int. Ed.*, 59, 1408-1428.
2. Wang, Y. et al. (2019), Organic crystalline materials in flexible electronics, *Chem. Soc. Rev.*, 48, 1492-1530.
3. Zhang, X., (2019), Precise Patterning of Organic Semiconductor Crystals for Integrated Device Applications, *Small*, 1900332, 1-20.

Catalytic transformation of methane to C1-C2

Prof. Junwang (John) Tang

Department of Chemical Engineering, University College London, UK, WC1E 7JE

*E-mail: junwang.tang@ucl.ac.uk

Abstract:
Methane hydrate/shale gas transformation is a potentially efficient pathway for both high value chemical production and renewable energy storage, thus has been attracting substantial interest over the last decades. However CH_4 activation is energy intensive and kinetically very challenging so that methane activation is regarded as the “holy grail” in the catalytically chemical process. [1] Photocatalysis provides a cost efficient potential to activation of such small molecule at very mild conditions, while to achieve the potential is a huge challenge.[2]

Stimulated by our recent research outcomes on the charge dynamics in inorganic semiconductor photocatalysis, which reveal that the low reaction efficiency is due to both fast charge recombination and large bandgap of an inorganic semiconductor [3], together with the recent findings on atomic catalysis [4], we developed novel material strategies for photocatalytic methane conversion to methanol and C2.

Highly dispersed atomic level iron species immobilised on a TiO_2 photocatalyst show an excellent activity for methane conversion, resulting into ~97% selectivity towards alcohols operated under ambient conditions by a one-step chemical process [5]. Such photocatalyst is also very stable, promising an attractive industrial process of methane upgrade. The dominating function of the iron species has also been investigated in detail. Furthermore, we designed a flow system for relatively efficient methane to C2, achieving the benchmark results in this area.[6]

Keywords: methane conversion, photocatalysis, single atomic catalylsis, hydrocarbons

References:

1. Li, X., Wang, C., Tang Tang, J. (2021) Progress and Challenges of Methane Transformation by Photocatalysis *Nature Rev. Mater.*, 2021. Accepted
2. Wang, Y., Vogel, A., Sachs, M., Sprick, R.S., Wilbraham,L., Moniz, S.J.A., Godin, R., Zwijnenburg, M.A., Durrant, J.R., Cooper, A.I., Tang, J. (2019) Current understanding and challenges of solar-driven hydrogen generation using polymeric photocatalysts, *Nature Energy,* 2019, 4, 746-760.
3. Tang, J., Durrant, J. R., & Klug, D. R. (2008). Mechanism of photocatalytic water splitting in TiO2. Reaction of water with photoholes, importance of charge carrier dynamics, and evidence for four-hole chemistry. *J. Am.Chem. Soc.*, *130*(42), 13885-13891.
4. Wang, A., Li, J., Zhang, T. (2018) Heterogeneous single-atom catalysis. *Nat. Rev. Chem.*, 2, 65-81.
5. Xie, J., Jin, R., Li, A., Bi, Y.,, Ruan, Q., Deng, Y., Zhang, Y., Yao, S., Sankar, G., Ma, D. , Tang, J. (2018) Highly Selective Oxidation of Methane to Methanol at Ambient Conditions by Titanium Dioxide-supported Iron Species, *Nature Catal.*, 2018, 1, 889-896
6. Li, X., Xie, J., Rao, H., Wang, C., Tang, J. (2020) Platinum and CuOx decorated TiO2 photocatalyst for oxidative coupling of methane to C2 hydrocarbons in a flow reactor., *Angew. Chem. Inter. Ed.*, 2020, 132, 19870-19875.

Material Computations for Energy Storage

Wei Lu [1,2]
[1] Department of Mechanical Engineering, University of Michigan, Ann Arbor, USA
[2] Department of Materials Science & Engineering, University of Michigan, Ann Arbor, USA

Abstract:

The electrification of the drivetrain is crucial to solve our energy problems and fill the gap to sustainable and zero emission mobility. We are now within reach of mass-marketed vehicles using Li-based batteries. Full engineering analysis of batteries and battery systems must be regularized, and engineering development is needed to allow creation of products and tools for integration of battery systems into vehicles. Electric vehicles and hybrid electric vehicles face significant battery-related challenges, including limited driving range and high battery cost resulting from the capacity fade of batteries during usage. The prediction of capacity fade and lifetime of batteries is important for cell design, determination of the optimal operation condition and control, and cell maintenance. Various mechanisms contribute to capacity fade. An integrated approach considering different aspects of the fading mechanisms is necessary. In this talk I will present some of our recent work in these areas, including a comprehensive capacity fade model and its experimental validation and application for battery optimization; a multiscale approach that couples mechanics and electrochemistry consistently at both particle and electrode scales which enables simulating various electrode phenomena, and its validation against explicit simulation of particle networks; and simulation of concurrent dendrite growth, SEI formation and penetration of lithium metal electrodes; and a new materials strategy to stop dendrite formation by a soft piezoelectric film. The materials strategy for improving the battery performance and application of machine learning for battery design will also be discussed.

Keywords: battery, simulation, mechanics, degradation, capacity, fracture, dendrite.

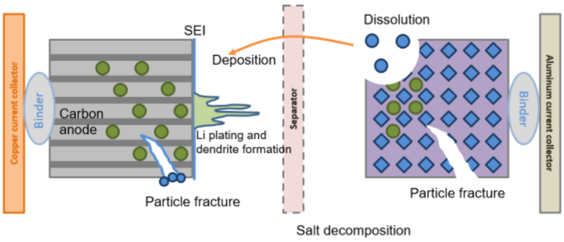


Figure 1: Degradation in a battery cell.

References:

1. Wu, B., Lu, W. (2019) A consistently coupled multiscale mechanical-electrochemical model with particle interaction and its validation, *J. Mech. Phys. Solids.*, 125, 89-111.

Novel platinum(II) complexes for light-emitting devices

F. Fagnani [1,*], A. Colombo [1], C. Dragonetti [1], D. Roberto [1], D. Marinotto [2], M. Cocchi [3]

[1] Dep. Chemistry, Università degli Studi di Milano and INSTM UdR Milano, Italy.
[2] CNR-SCITEC, Milan, Italy.
[3] CNR-ISOF, Bologna, Italy.

Abstract:

There has been intense activity in the design of transition metal complexes as phosphors for organic light-emitting devices (OLEDs). As a matter of fact, the high intersystem crossing induced by the metal ion promotes emission from the otherwise wasted triplet states, which represent up to 75% of the excited states formed upon charge recombination in an electroluminescent device. Particularly charming are Pt(II) complexes, due to the parallel emissions from bi- and mono-molecular excited states, which allow tuning of the efficiency and color of OLEDs.[1] Among them, cyclometalated 1,3-di(2-pyridyl)benzene Pt(II) chloride complexes are fascinating. They are very bright emitters, in solution at room temperature, and their emission color can be modulated through introduction of substituents on the pyridyl or benzene rings.[1] Surprisingly, the effect of the co-ligand on their emissive properties has not been well studied yet. A few years ago it was observed that replacement of chloride by arenethiolate (–SPhR) leads to low quantum yields.[2]

However, we recently found that [Pt(5-mesityl-1,3-di-(2-pyridyl)benzene)(1-phenyl-1H-tetrazole-5-thiolate)] (**1**; Figure 1) is highly emissive and has an excellent solubility, being the first member of a new family of platinum emitters useful for the preparation of efficient solution-processable OLEDs.[3]

This observation prompted us to prepare other members of this appealing family, by replacement of mesityl with other substituents such as methyl (**2**) and 2-thienyl (**3**). We also investigated the use of another sulphur-donor ligand, 4-phenylthiazole-2-thiolate. Thus, various [Pt(5-X-1,3-di-(2-pyridyl)benzene)(4-phenylthiazole-2-thiolate)] complexes (X = mesityl (**4**), methyl (**5**), 2-thienyl (**6**), 4-(diphenylamino)phenyl (**7**)) were prepared. All these Pt(II) complexes are highly emissive in CH_2Cl_2 solution, the color of the emission being modulated by the nature of the substituent at the 5 position of 1,3-di-(2-pyridyl)benzene. Particularly fascinating is complex **6**, which presents the highest quantum yield and can be used for the preparation of convenient solution-processable OLEDs. The results on these novel Pt(II) complexes will be presented.

Keywords: platinum complexes, luminescence, OLEDs.

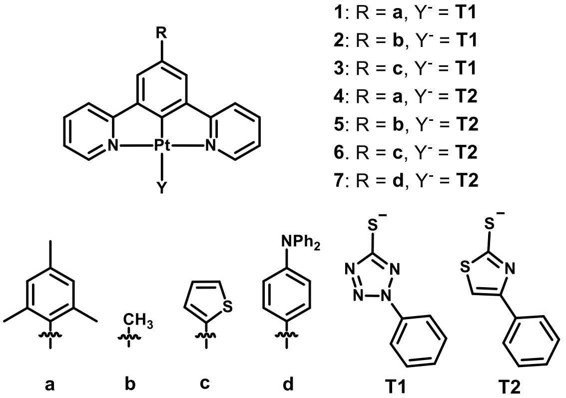


Figure 1: Structure of the investigated Pt(II) complexes.

References:

1. Kalinowski, J., Fattori, V., Cocchi, M., Williams, J.A.G. (2011), Light-emitting devices based on organometallic platinum complexes as emitters, *Coord. Chem. Rev.*, 255, 2401-2425.
2. Tarran, W.A., Freeman, G.R., Murphy, L., Benham, A.M., Kataky, R., Williams, J.A.G. (2014), Platinum(II) complexes of N^C^N-coordinating 1,3-bis(2-pyridyl)benzene ligands: thiolate coligands lead to strong red luminescence from charge-transfer states, *Inorg. Chem.*, 53, 5738-5749.
3. Dragonetti, C., Fagnani, F., Marinotto, D., di Biase, A., Roberto, D., Cocchi, M., Fantacci, S., Colombo, A. (2020), First member of an appealing class of cyclometalated 1,3-di-(2-pyridyl)benzene platinum(II) complexes for solution-processable OLEDs, *J. Mater. Chem. C,* 8, 7873-7881.

Pixelated Smart Window for High Dynamic Range Signage Displaying Applications

Qihao Jin[1,*], Qiaoshuang Zhang[1], Junchi Chen[1], Tim Gehring[1], Santiago Eizaguirre[1], Robert Huber[1], Guillaume Gomard[1,2,3], Uli Lemmer[1,2], Rainer Kling[1]
[1] Light Technology Institute, Karlsruhe Institute of Technology, Karlsruhe, Germany
[2] Institute of Microstructure Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany
[3] Carl Zeiss AG, Hermann-von-Helmholtz-Platz 6, 76344 Eggenstein-Leopoldshafen, Germany

Abstract:

Smart windows have been intensively investigated for energy and light management during the last decades. Mechanoresponsive smart windows are one of the research hot spots because of their energy-saving operation and cost-effective fabrication. To introduce a displaying functionality in such smart windows can open various application scenarios and dramatically reduce energy consumption in daily signage displays. However, the optical properties in conventional mechanoresponsive smart windows are usually modulated globally. Therefore, a pixelated smart window is expected to realize a smart-window-based signage display. In this work, we demonstrate a pixelated mechanoresponsive smart window, which can display images in a high dynamic range. The surface pixelation was achieved by a newly developed surface hydrophilization method, inkjet-printed micro-etching-mask, and plasma surface treatment. Compared to the traditional mechanoresponsive smart windows, a linear haze tunability was achieved without applying strain. Therefore, a two-dimensional haze modulation was realized, namely mechanoresponsivity upon strain and haze tunability in a static state. Furthermore, the fully controllable haze property leads to a 225 haze depth in the smart window, displaying the image in a high dynamic range. To the best of our knowledge, this is the first demonstration of a pixelated mechanoresponsive smart window, which can be used in signage displays. Moreover, the developed fabrication processes show high versatility and can be utilized in universal surface treatment.

Keywords: smart window, display, surface hydrophilization, inkjet printing, high dynamic range, light scattering

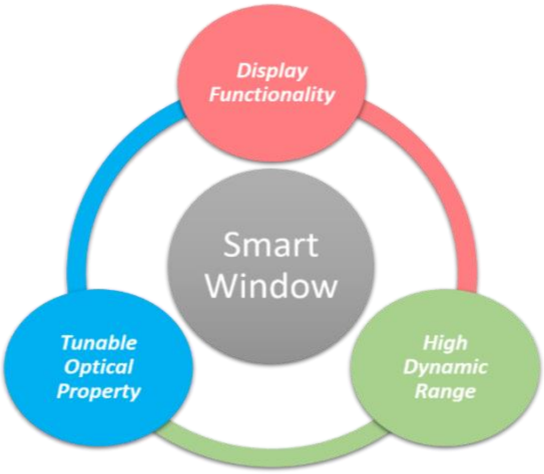


Figure 1: Illustration of the core concept of the work. The display functionality and tunable optical property are integrated into a smart window to present images in a high dynamic range.

Telomeric DNA Fragments and Carbon Nanotubes as pH Controlled Carriers of Doxorubicin. Molecular Level Analysis.

T. Panczyk
Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences
ul. Niezapominajek 8, 30238 Krakow, Poland

Abstract:

The pH controlled folding/unfolding property of DNA i-motif sequences can be utilized in various areas of science and particularly in nanomedicine. Indeed, there were proposed many interesting applications of DNA i-motifs as sensors, nanomachines or drug delivery/controlled release platforms. [1,2] In this study we are going to show how the cytosine rich fragments interact with carbon nanotubes and doxorubicin (DOX) and that it is possible to engineer an interesting pH-controlled carrier of doxorubicin in that way.

Our predictions are based on the application of molecular dynamics simulations with the adequately chosen force fields for each component of the system. We can see that at neutral pH and without DOX in the simulation box, the i-motif precursors are weakly bound to the nanotube surface or they are able to detach and stay as individual molecules in solution, Fig. 1A. However, in the presence of DOX the i-motif precursor and DOX molecules intercalate each other and the whole object attach to the nanotube surface, Fig. 1B. Deeper analysis of that structure led to the conclusion that this is very stable structure and DOX molecules are immobilized within the network of nucleic acid sequences. Analysis of the system at the acidic pH led to the conclusion that binding of i-motifs has been weakened when compared to their random coil counterparts. This applied either to the case without DOX molecules, Fig. 1C, or to the mixed system containing DOX and i-motifs adsorbed on the nanotube sidewall simultaneously. Further analysis of energetic factors confirmed that the state in Fig. 1D is much less stable than the state in Fig. 1B and after macroscopic time DOX molecules would be released from the structure Fig. 1D spontaneously.

The results summarized above imply that DOX can be effectively immobilized on the nanotube surface at the neutral pH when the (CCCTAA)n nucleic acid sequences are also present in solution. This structure can realize pH triggered release of DOX in tumor microenvironment.

Keywords: i-motif, carbon nanotube, doxorubicin, drug delivery

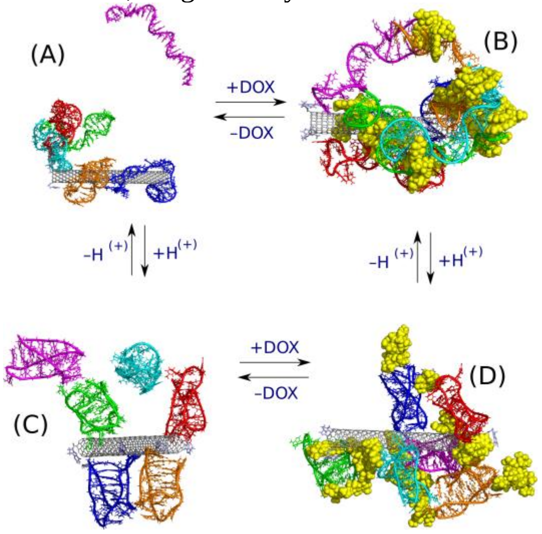


Figure 1: Optimal configurations of the mixed systems: carbon nanotube, (CCCTAA)4 nucleic acid sequence and doxorubicin found in molecular dynamics simulations at various pH conditions.

Acknowledgment:

This work was supported by Polish National Science Centre grant 2017/27/B/ST4/00108.

References:

1. Xu, C., Zhao, C., Ren, J., Qu, X. (2011) *Chem. Commun.* 47, 8043.
2. Wolski, P., Nieszporek, K., Panczyk, T. (2020) *International Journal of Molecular Sciences*, 21, 3619.

Ionic Liquids as a green tool for melanin manipulation at the nanoscale: nanotechnological perspectives

M. Ambrico[1*], P. Manini[2], L. Guazzelli[3], A. Mezzetta[3], L. Valgimigli,[4] P.F. Ambrico[1], T. Ligonzo[5]
and M. d'Ischia[2]

[1]CNR– Istituto per la Scienza e Tecnologia dei Plasmi, Bari, Italy
[2]Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Napoli, Italy
[3]Dipartimento di Farmacia, Universita'degli Studi di Pisa, Pisa, Italy
[4]Dipartimento di Chimica "G. Ciamician",Universitàdi Bologna, Bologna,Italy
[5]Dipartimento Interateneo di Fisica, Università degli Studi di Bari, Bari, Italy

Abstract:
The control of the antioxidant and redox properties of nanosized biomaterials stands today as one of the relevant scores in nanosciences for biological applications. In nanomedicine, the tunability of physicochemical properties is highly required for drug delivery and control of the inflammatory diseases-mediated oxidative stress including cancer. However, such applications need to be as safe as possible with limited side effects due to the residual circulating nanoparticles in living organisms, as occurring in the case of heavy metal nanoparticles.

In recent years, the black insoluble eumelanin pigments from human skin and eyes, has attracted interest as possible bio-friendly candidates because of easy redox properties modulation. Among them, polydopamine nanoparticles (PDA NPs) attract considerable interest dueto their high biocompatibility for nanobiological applications, including theranostics. Besides beingapproved by the USA food and drug administration, PDA NPsexhibit enhanced drug loading capacity with respect to metallic nanovectors allowing increased drug efficiency during release and limiting side effects. Recently, new interesting and intriguing opportunities in PDA research have derived from the discovery that ionic liquids (ILs) are capable of disassembling PDA aggregate to the nanoscale level. EPR data demonstrated that ILs establish specific interactions with the free radical centres on PDA surface thus modulating the spin environment and populations in NPs. As a further investigation, it wasof interest to assess whether de-aggregation in ILs affects the redox activity of PDA NPs besides the EPR propertiesvia IL-mediated mechanisms.

In this study we overview the impact of structural controland surface –IL interactions on the IL-dependent redox activity of PDA NPs. By combining broadband dielectric and impedance spectroscopy results with EPR investigations wereport a remarkable correlation between the features at free radical centres. These results may dictate design rules for new and safer functional nanovectors for drug and theranostics applications.

Keywords: Polydopamine; electrical impedance spectroscopy; electron paramagnetic resonance spectroscopy; ionic liquids; nanovectors

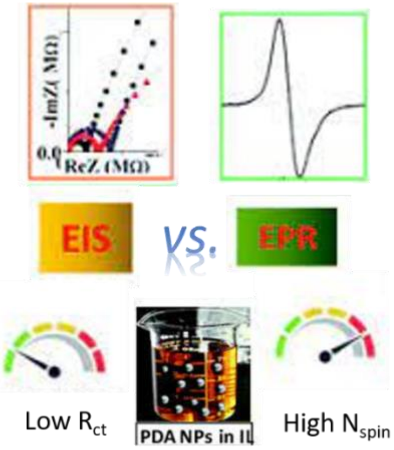


Figure 1: Simplified sketches illustrating the PDA suspension in ILs and the main results correlating EIS (charge transfer resistance, R$_{ct}$) vs. EPR (N$_{spin}$ /L density)

References:

1. Manini, P.; Margari, P.; Pomelli, C. S.; Franchi, P.; Gentile, G.; Napolitano, A.; Valgimigli, L.; Chiappe, C.; Ball, V.; D'Ischia, M. NanoscaleDisassembly and Free Radical Reorganization of Polydopamine in IonicLiquids. J. Phys. Chem. B 2016, 120, 11942-11950, doi:10.1021/acs.jpcb.6b08835.Montoneri, 471-491.
2. Ambrico M, Manini P, Ambrico PF, et al. Nanoscale PDA disassembly in ionic liquids: Structure-property relationships underpinning redox tuning. Phys Chem Chem Phys. 2019;21(23):12380-12388

Innovative virtual approach for treatment of fears and enhancement of cognitive abilities

G.Scavone[1*], D.Benatti[1], M.Donadio[1], A.Ruoto[2], D. Sinitò[2], E. Massa[2], V. Santarcangelo[2]

[1] Centro Rham Srl, Matera, Italy
[2] iInformatica Srl, Trapani, Italy

Abstract:

Research and development activities carried out by Centro Rham Srl together with innovative PMI iInformatica concerned the design and experimental prototyping of innovative sceneries for the treatment of fears using virtual reality headsets in conjunction with the use of binaural audios and biofeedback-monitoring devices. This wearable device is a prototypical headset that allows to manage sceneries together with audios characterized by pink noise (relaxing) components and binaural beats (alfa, theta, delta) aimed at a therapeutical treating of phobias. Thanks to spectrogram analysis it is possible to understand the frequency and intensity components that characterize a certain acoustic stimulus, with the aim, together with a tactile/visual aid, to evoke a cognitive response. Biofeedback is acquired and monitored in real time using more wearable sensors. Research also concerned digital sceneries and tactile devices prototyping for an upgrade of cognitive abilities. This prototypical acoustical-sensorial experience is given by the union of binaural audios focused on the improvement of mnemonic abilities together with the use of cards and of an haptic pneumatical matrix to stimulate different cognitive functions of orientation (temporal and spatial), attention (visive and tactile), memory (visuospatial, visive-for related objects, episodic and associative), logic and reasoning (correlation with acoustic and tactile inputs). Furthermore, the spectrogram analysis is fundamental for lexical and phonetic analysis.

Keywords: biofeedback, acustic experience, fear treatments, binaural beats

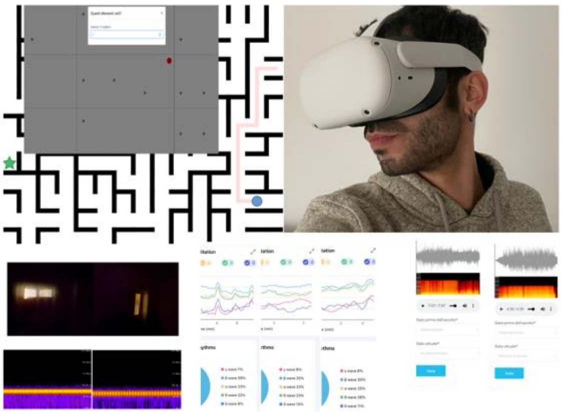


Figure 1: The figure shows virtual reality devices combined with binaural audios for the treatment of phobias and to an improvement of cognitive abilities monitored through neuro-feedback

Figure 2: The figure shows the Ricorda box, implemented experimental prototype

References:

1. Scavone, G. (2020), Uno strumento ludico-formativo volto alla stimolazione sensoriale e al supporto per lo stimolo e il recupero di alcune funzioni cognitive, UIBM. Patent P. n. 202020000007130
2. Scavone, G. (2019), Intelligent systems to support patients, ASA

Sensors 2021 Virtual Session

Applications of Graphene Modified Electrodes

S. Pruneanu*, F. Pogacean, C. Varodi, M. Coros, L. Magerusan, V. Mirel, and A. Ciorita

National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103
Donat street, 400293, Cluj-Napoca, Romania
E-mail: stela.pruneanu@itim-cj.ro

Abstract:

Graphene may be synthesized by various methods such as chemical vapor deposition, mechanical exfoliation of graphite powder, chemical or microwave synthesis. There are always some important parameters that should be considered, such as the production cost, scalability, reproducibility and the quality of the obtained materials. Among the previously reported methods, the synthesis of graphene by electrochemical exfoliation of graphite rods brings several advantages. We can mention the cheap electrolytes generally used (acidic or salts solutions), ambient synthesis conditions and the preservation of the highly conductive sp^2 structure of graphite.

Screen-printed electrodes (SPE) are preffered over traditional glassy carbon substrates, due to the possibility of mass production and the facility to be attached to a portable device for in-situ applications. Moreover, the carbon inks used to imprint the working electrode can be modify with different materials or molecules for biomedical analyses [1]. A typical screen-printed electrode contains the counter, the working and the reference electrode on the same substrate (Figure 1). Generally, a volume of 60 μL of analyte is enough for running the electrochemical experiments.

8-hydroxy-2'-deoxyguanosine (8-OHdG) is one of the bio-markers used for the evaluation of oxidative damage in DNA [2]. Its accumulation has been reported in cancerous tissues, polycystic ovary syndrome, leukemia [4], or in chronic and aggressive periodontitis [5]. In this work we tested the electrochemical performances of screen-printed electrodes modified with graphene towards 8-OHdG detection, both in standard laboratory solutions (pH 6 PBS) and in human saliva. The results were compared with those of unmodified SPE.

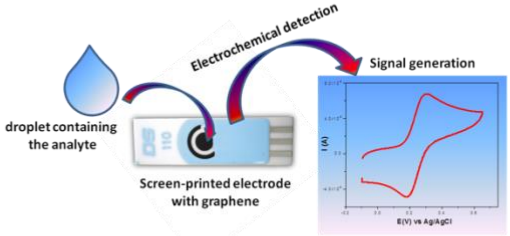


Figure 1: Screen-printed electrode modified with graphene for the detection of 8-OHdG

Keywords: *graphene-modified electrodes, biomolecules detection, electrochemical sensors.*

References:

1. Dorledo de Faria, R.A.; Messaddeq, Y.; Heneine, G.D.; Matencio, T. (2019) Application of screen-printed carbon electrode as an electrochemical transducer in biosensors. *Int. J. Biosens. Bioelectron.*, 5, 1–2.
2. Varodi C.; Pogacean F.; Coros M., Rosu M-C.; Stefan van Staden R-I.; Gal E.; Barbu-Tudoran L.; Pruneanu S.; Mirel S., (2019), Detection of 8-Hydroxy-2'-Deoxyguanosine Biomarker with a Screen-Printed Electrode Modified with Graphene, *Sensors*, 19, 4297
3. Zhang, P.; Lian, K.;Wu, X.; Yao, M.; Lu, X.; Kang,W.; Jiang, L. (2014). Evaluation of the oxidative deoxyribonucleic acid damage biomarker 8-hydroxy-2'-deoxyguanosine in the urine of leukemic children by micellar electrokinetic capillary chromatography. *J. Chromatogr. A* 1336, 112–119.
4. Buduneli, N., (2019) Biomarkers in saliva and serum samples for periodontal disease and interactions with systemic health. *Curr. Oral Heal. Reports*, 6, 31–36.

Ackowledgement: *This work was supported by grants of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number* PN-III-P4-ID-PCCF-2016-0006 and project 500PED/2021, *within PNCDI III.*

Validation of data from an artificial sniffer dog by common analytical techniques.

I. Hardy [1*], M. H. Jakobsen [2], T. Treiberg [2], C. H. Gotfredsen [2], E. Dossi [1]

[1] Centre of Defence Chemistry, Cranfield University, Shrivenham, England
[2] Department of Chemistry, Technical University of Denmark, Lyngby, Denmark

Abstract:

Chemicals can be detected and identified by using their specific molecular properties combined with a variety of smart-advanced technologies.[1] In this work, the interaction of illicit chemicals and chromic dyes have been studied using a set of common analytical techniques with the aim to validate data generated from detection experiments using CRIM-TRACK, an artificial sniffer dog. The CRIM-TRACK detection is based on a colorimetric sensor system that monitors chromic dyes changing color when in contact with the vapors of illicit molecules (Analytes).[2,3]

The color change mechanism attributed to the analyte-dye interaction, was investigated by Proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy interfaced with Ultraviolet-Visible (UV-Vis) spectrophotometry. Specifically, for phenylacetone (BMK), a precursor chemical of methamphetamines, the hydrogen bonding which occurs between the BMK and dye molecules was revealed by ^{1}H NMR. This was confirmed by UV-Vis where a shift in absorption wavelength and/or a change in absorbance of $\pi \rightarrow \pi^*$ transitions occurred. Hexamine, an explosives precursor, was found to form hydrogen bonding or ion pairs with specific families of dyes. The data are currently examined using complementary analytical techniques such as Fourier Transform Infrared spectroscopy and X-Ray Powder Diffraction crystallography.

The gained data are used for i) validating of the CRIM-TRACK detection results, ii) identifying and understanding the analyte-dye interaction and detection mechanism and iii) quick pre-screening of potential "reactive dyes" for the colorimetric CRIM-TRACK sensor.

Keywords: NMR spectroscopy, UV-Vis spectrophotometry, illicit chemicals detection, colorimetric sensors, CRIM-TRACK sniffer system

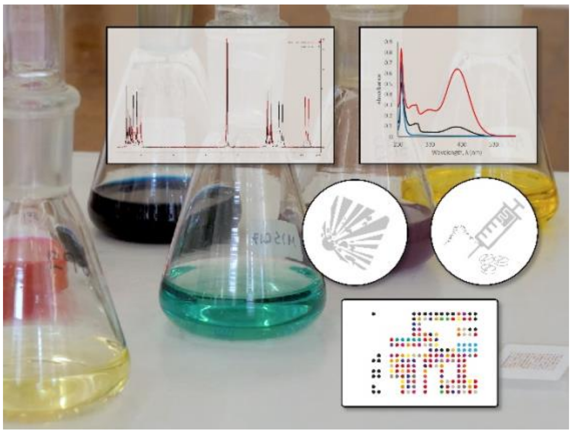


Figure 1 Background: dyes used in the CRIM-TRACK colorimetric sensor. Bottom right: Schematic representation of CRIM-TRACK colorimetric microchip. Middle right: Illicit substances symbols: explosives and controlled drugs. Top left: ^{1}H NMR spectra of dye (black line) and Hexamine-dye (Red line). Top right: UV Vis spectra of Hexamine (Blue line), dye (Black line) and Hexamine-dye mixture (Red line).

References:

1. Klapec, D. J.; Czarnopys, G.; Pannuto, J. (2020), *Forensic Sci. Int. Synerg.*, 2, 1–31. https://doi.org/10.1016/j.fsisyn.2020.01.020.
2. Mølgaard, L. L. et al (2017) *Proc. SPIE 10183, Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XVIII,* 1018307. https://doi.org/10.1117/12.2262468
3. Munk, J. K. et al (2015) *Proc. SPIE 9652, Optics and Photonics for Counterterrorism, Crime Fighting, and Defence XI; and Optical Materials and Biomaterials in Security and Defence Systems Technology XII,* 965208 https://doi.org/10.1117/12.2194915

pH sensor using silver nanoparticles embedded in silica-coated optical fibres

S. Debnath [1], Y-C. Chen [1], T. Green [1], G. Hinds [2], S. Roy [1]
[1]Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, United Kingdom, G1 1XL
[2]National Physical Laboratory, Hampton Road, Teddington, United Kingdom, TW11 0LW

Abstract:
Quantifying hydrogen ion concentration in solution (or pH) has important applications in different industries. However, measurement of pH at high temperature and pressure (HTHP) remains a significant challenge, due to lack of reliable instrumentation. Recent studies on the surface plasmon resonance (SPR) of gold nanoparticles coated on optical fibres exhibited sensitivity to pH in solutions at different temperatures and pressures [1,2]. Since optical fibres are stable under HTHP conditions, these findings indicate a potential way forward to develop pH sensors capable of operating in such environments.

This work reports on the development of silver nanoparticle embedded silica (SiO_2) coatings on optical fibres. The coatings were prepared using the sol-gel technique by adding tetraethoxysilane (TEOS) to ethanol, water and silver nitrate. In order to determine the optimum conditions for formation of a gel with good adhesiveness on glass, while containing sufficient silver nanoparticles for pH sensitivity, experiments were carried out by coating glass slides (Fisher Scientific, 26 mm × 76 mm × 1.2 mm) at different temperatures and reaction times as shown in Figure 1(a).

It was observed that gel formation at 35 °C for 48 hours showed good adhesiveness with glass. After preparing the gel, glass slides were then dip-coated and dried in an oven at 200 ºC for 2.5 hours, where silver ions were reduced to form silver nanoparticles. Characterization of the coating using Ultraviolet/Visible (UV-Vis) spectroscopy as shown in Figure 1(b) showed an absorbance peak at around 400 nm, which is consistent with the presence of silver nanoparticles [3].

Once the preparation method had been established, a piece of optical fibre was etched in 7 M NaOH to remove the outer coating and cladding, before being coated with the gel as shown in Figure 1(c). The coated optical fibre was observed under a high-resolution microscope and was found to have 5-6 microns of the coating around the core of the fibre. Ongoing experiments are focused on connecting these fibres to a light source and UV-Vis spectrophotometer and measuring absorbances in solutions of different pH, which will be reported at the meeting.

Keywords: pH sensor, silver nanoparticles, sol-gel technique.

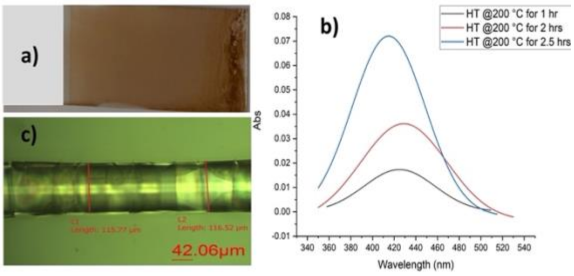


Figure 1: a) Silver nanoparticle/TEOS coating on a glass slide heat-treated at 200 °C for 2.5 hours; b) UV-Vis spectra of coated glass slides for samples heat-treated at 200 °C for 1, 2 and 2.5 hours, showing an absorption peak near 400nm, indicating the formation of silver nanoparticles; and c) Silver nanoparticle/TEOS coating on the core of an optical fibre.

References:

1. Wang, C., Ohodnicki, P.R., Su, X., Keller, M., Brown, T.D., Baltrusa, J.P. (2015) Novel silica surface charge density mediated control of the optical properties of embedded optically active materials and its application for fiber optic pH sensing at elevated temperatures, *Nanoscale*, 7, 2527–2535.
2. Wang, C., Su, X., Brown, T.D., Ohodnicki, P.R. (2015) Novel sensing materials for harsh environment subsurface pH sensing applications, *Proc. of SPIE*, 9480, 1–6.
3. Agnihotri, S., Mukherji, S., Mukherji, S. (2014) Size-controlled silver nanoparticles synthesized over the range 5–100 nm using the same protocol and their antibacterial efficacy, *RSC Advances*, 4(8), 3974–3983.

Rapid, Cost-Effective, and Intelligible Bi-Electrode Electrochemical Sensing System for Detection of Attomole-Level Dengue Virus Sequence

T. Agarkar [1,*], S. Ghosh [2], A. Kumar [1]

[1] Department of Physics, Bennett University, Greater Noida (U.P.), India
[2] Department of Chemistry, Bennett University, Greater Noida (U.P.), India

Abstract:
DNA amplification detection is typically a lengthy and sophisticated procedure involving high-end instrumentation. Electrochemical detection has recently opened a low budget, straightforward and speedy method for detection with the aid of an electrochemically active redox probe. It characteristically employs a tri-electrode geometry for sensing involving standard reference electrode usually made of a noble metal that adds-up the cost of detection. This work proposes a novel approach for the rapid detection of dengue virus sequence DNA amplification using a bi-electrode sensing geometry using a cost-effective and scalable sensing electrode. The sensing layer of metal oxide semiconductor is physically probed to tune its electronic state in order to regulate the electrochemical sensing signal. The fabricated device has reduced the sensing time to 20 minutes and the limit of detection is achieved to a value as low as 2 attomole of initial DNA concentration.

Keywords: Electrochemical detection, metal oxide, redox probe, sol-gel spin coating.

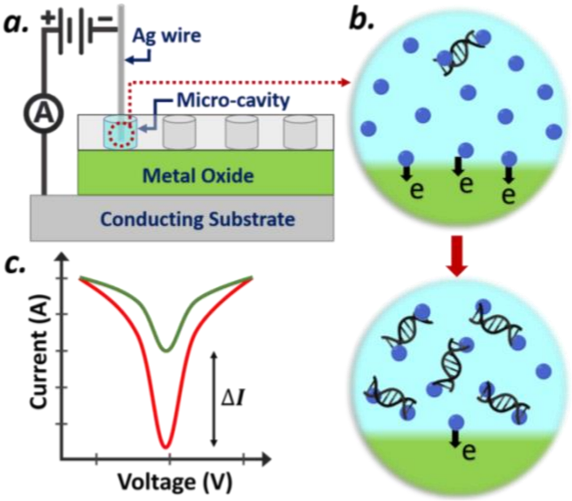


Figure 1: **a.** Schematic of the bi-electrode sensing geometry with micro-cavity to hold the electrolyte; **b.** Reduction in redox probe density (represented by blue circles) after DNA amplification that implies lower charge transfer at electrode-electrolyte interface; **c.** Schematic representation of sensing signal showing reduced peak height post DNA amplification.

References:

1. Tsaloglou, M. N., Nemiroski, A., Camci-Unal, G., Christodouleas, D. C., Murray, L. P., Connelly, J. T., Whitesides, G. M. (2018), Handheld Isothermal Amplification and Electrochemical Detection of DNA in Resource-Limited Settings, Anal. Biochem., 543, 116–121.

2. Nagatani, N., Yamanaka, K., Saito, M., Koketsu, R., Sasaki, T., Ikuta, K., Miyahara, T., Tamiya, E. (2011), Semi-Real Time Electrochemical Monitoring for Influenza Virus RNA by Reverse Transcription Loop-Mediated Isothermal Amplification Using a USB Powered Portable Potentiostat. Analyst, 136 (24), 5143–5150.

Widening the Range of Trackable Environmental and Health Pollutants for Li-Garnet-Based Sensors

M. Balaish[1], J. L.M. Rupp [1,2,*]

[1]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[2]Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139, US

Abstract:

Classic chemical sensors integrated in phones, vehicles, and industrial plants monitor the levels of humidity or carbonaceous/oxygen species to track environmental changes. According to current projections, the gas sensor market is estimated to grow at an annual rate of 7% between 2021-2026 (valued at USD 1.5 billion by 2026). [1] The projections indicate the strong need to increase the ability of sensors to sense a wider range of chemicals for future electronics not only to continue monitoring environmental changes but also to ensure the health and safety of humans. To achieve this goal, more chemical sensing principles and hardware must be developed. The critical factors that determine the sensing performance for rather corrosive toxins such as SO_2 are to develop a suitable electrochemistry and sensor material selection stable in this environment, and operating at low temperature (ideally below 300 °C) to assure a low energy footprint per sensing device volume. We propose in this work as a promising alternative cubic Li-garnet $Li_7La_3Zr_2O_{12}$ (LLZO) as a solid-state electrolyte for new SO_2 sensors due to their three orders of magnitude increased ionic conductivity (~mS cm^{-1}) and higher electrochemical stability window, which allows a wider definition and choice for sensing material electrodes. The material class of Li-garnets is known for about a decade[2,3] and has proven success for solid state batteries, however, it had only recently been introduced to serve as electrolyte for type III sensors tracking less corrosive gases such as CO_2 with fast sensing and recovery times.[4,5]

Here, we provide a proof-of-principle for the specific electrochemistry, material selection, and design of a Li-garnet LLZO-based electrochemical sensor, targeting the highly corrosive environmental pollutant sulfur dioxide (SO_2). [6][7] For that, we explore the following sensor electrochemistry $2Li^+ + SO_3 + 0.5O_2 + 2e^- \leftrightarrow Li_2SO_4$ and investigated the major aspects that affect the electromotive force response according to the Nernstian behavior and the response/recovery time of the sensor, explicitly the auxiliary sensing electrode composition and microstructure. Novel composite sensing electrode designs using LLZO based on porous scaffold, employed to define a high number of reaction sites, allowed to successfully track SO_2 at the dangerous levels of 0–10 ppm with close-to-theoretical SO_2 sensitivity. The introduction of the composite sensing electrode Li_2SO_4–$CaSO_4$–LLZO with the LLZO electrolyte conductor achieved close-to-theoretical sensitivity of 47.7 mV/dec at remarkably low operating temperature of the sensor of 240 °C. We wish to highlight that this outperforms previously reported SO_2 type III electrochemical sensors operating on Zr^{4+} (400 °C) or Na^+ (600 °C) ion-conducting solid electrolytes in terms of their operation temperature and has as a consequence impact on the sensor power consumption.

Keywords: SO_2 gas sensor, potentiometric sensors, Li garnet $Li_7La_3Zr_2O_{12}$, sensing electrode.

References:

[1] MarketsandMarkets^{TM}, Gas Sensors Market by Analysis, Type, Technology, Technology, Output Type, Product Type, Application| COVID-19 Impact Analysis, **2021**.

[2] M. Balaish, J. C. Gonzalez-Rosillo, K. J. Kim, Y. Zhu, J. D. Hood, J. L. M. Rupp, *Nat. Energy* **2021**.

[3] J. L. M. Zhu, Y; Gonzalez-Rosillo, J C; Balaish, M; Hood, Z D; Kim, K J; Rupp, *Nat. Rev. Mater.* **2020**.

[4] Y. Zhu, V. Thangadurai, W. Weppner, *Sensors Actuators, B Chem.* **2013**, *176*, 284.

[5] M. Struzik, I. Garbayo, R. Pfenninger, J. L. M. Rupp, *Adv. Mater.* **2018**, *30*, 1.

[6] M. Balaish, J. L. M. Rupp, *Adv. Mater.* **2021,** DOI 10.1002/(ISSN)1521-4095.

[7] M. Balaish, Z. D. H. Hood, J. Rupp, Gas sensor device containing Lithium garnet **2021,** provisional application 63/154,336.

New illumination / sensing platform

R. Trihan [1,*], A. Aimable [1], F. Rossignol [1], J. Kowalko [2], H. Węglarz [2], A. Szysiak [2], A. Kozłowska [2], B. Fetliński [3], B. Janaszek [3], M. Kaczkan [3], M. Ihle [4], S. Ziesche [4], P. Giemza [5], M. Szczypa [5]

[1] IRCER – Institute of Research for Ceramics (Limoges, FRANCE)
[2] Łukasiewicz Research Network – Institute of Microelectronics and Photonics (Warsaw, POLAND)
[3] Institute of Microelectronics and Optoelectronics WUT (Warsaw, POLAND)
[4] Fraunhofer IKTS – Institute for Ceramic Technologies and Systems (Dresden, GERMANY)
[5] Teknosystem Co. Ltd (Warsaw, POLAND)

Abstract:

This research study focuses on the development of a new optical sensor platform. The device is based on a layered doped transparent ceramic pumped with a laser diode and coupled with a functionalized surface plasmon resonance (SPR) structure as an innovative photonic component for both lighting and sensing. Targeted areas are the detection of pollutants in water (Cu, Fe, etc.) or air (CO, NOx, etc.), as well as medical diagnosis.

The core of the lighting component is a doped YAG ceramic, adapted to the desired optical properties, under LED excitation. Light enhancement occurs at the device surface due to the SPR effect (Figure 1) for noble metal nanoparticles (Figure 2). For that purpose, the SPR effect can also be obtained by adding hybrid Au@SiO_2 or Ag@SiO_2 nanoparticles (NPs) to form sensing layers on the optical component. In addition, a functionalized mesoporous silica top-coat is also deposited according to the targeted chemical or biological compound.

The presentation will focus on surface functionalization (nanoparticles synthesis, deposition on the surface, mesoporous silica top-coat elaboration) and detection capabilities through optical measurements based upon a demonstrator.

Keywords: silica-based materials, mesoporous silica, Surface Plasmon Resonance (SPR), gold/silver nanoparticles, YAG ceramics, surface functionalization, surface coating, deposition methods, pollutants detection, medical diagnosis.

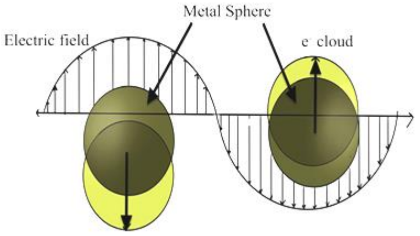
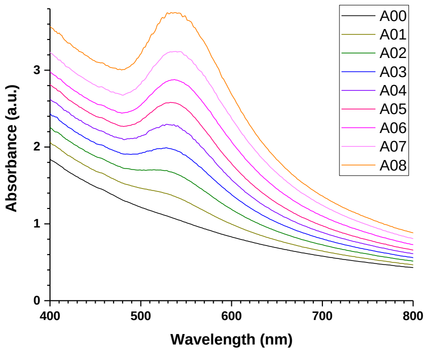


Figure 1: Surface Plasmon Resonance (SPR) effect occurring for noble metal NPs. Electrons from the conduction band are oscillating due to resonance with light energy waves. [1]



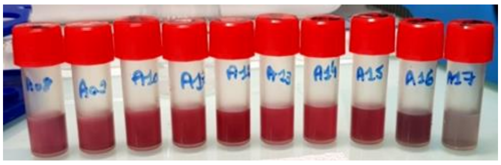


Figure 2: Example of colored nanoparticles solutions depending on the NPs size. [2]

References:

1. Upadhyaya, A. and Rincón, G. (2019) Visible-Light-Active Noble-Metal Photocatalysts for Water Disinfection: A Review. *Journal of Water Resource and Protection*, **11**, 1207-1232.
2. Agnihotri, S., Mukherji, S. and Mukherji, S. (2014) Size-controlled silver nanoparticles synthesized over the range 5-100 nm using the same protocol and their antibacterial efficacy. *Royal Society of Chemistry*, **4**, 3974-3983.

BTEX Detection: Merging MEMS Technology with Metal Ion-Functionalized Au MPCs to Exploit Cation-π Interactions

P. K. Adhihetty [1], S. Halder [2], D. M. Smith [1], X. Fu[2*], M. H. Nantz[1*]

Departments of [1]Chemistry and [2]Chemical Engineering, University of Louisville, Louisville, KY 40292 USA
[*]Corresponding authors: michael.nantz@louisville.edu and xiaoan.fu@louisville.edu

Abstract:

Organic-based chemiresistors are used as gas sensors to detect harmful volatile organic compounds (VOCs) in polluted air. Much effort has been devoted toward developing chemiresistors capable of sensing aromatic VOCs.[1] However, current approaches to detect aromatic VOCs are not highly sensitive or selective at ambient temperature. We seek to develop organic-based chemiresistors to detect trace levels of benzene, toluene, ethyl benzene and xylene (BTEX) in outdoor and indoor air. In our study, the designed sensors (Figure 1) consist of interdigitated electrodes (IDEs), designed using microelectromechanical systems (MEMS), coated with thiolate monolayer-protected gold clusters (Au MPCs). The surfaces of the synthesized thiolate-protected Au MPCs are functionalized with metal cations bound to carboxylate ions.[2,3] We sought to exploit the strong cation-π noncovalent interactions between cations of the sensor and the π-systems of BTEX as a sensing mechanism. In this study, thiolate-coated Au MPCs with ~2 nm particle diameter were synthesized using *N*-Boc protected short alkane chain (6C) and long alkane chain (11C) aminooxy thiols via the two phase Brust-Schiffrin method.[4] Chemiresistors fitted with motifs to enable rapid screening of multiple motifs were prepared using an oxime ether coupling approach. Furthermore, 4-mercaptobenzoic acid was also used to synthesize Au MPCs. Subsequently, the alkali metal ions Li^+, Na^+, K^+, Rb^+, Cs^+ as well as ammonium ions were incorporated at the surface of the Au MPCs. Herein, we present the aromatic VOCs sensing ability of the chemiresistors derived from cation-functionalized thiol-coated Au MPCs.

Keywords: chemiresistor, cation-functionalized Au MPCs, IDEs, cation-π interaction

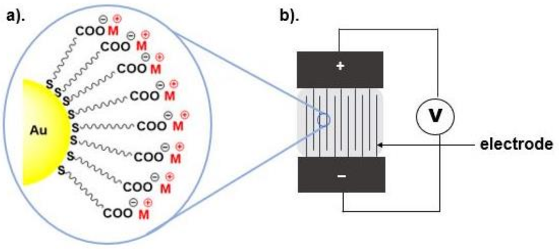


Figure 1. (a) Metal ion carboxylate-functionalized Au MPCs. (M^+ = metal ion); (b) structure of the chemiresistor with interdigitated electrodes

References:

1. Han, L., Shi, X., Wu, W., Kirk, F. L., Luo, J., Wang, L., Mott, D., Cousineau, L., Lim, S. I. I., Lu, S., Zhong, C. J. (2005) Nanoparticle-structured sensing array materials and pattern recognition for VOC detection, *Sensors and Actuators B*, 106, 431-441.
2. Leopold, M. C., Donkers, R. L., Georganopoulou, D., Fisher, M.; Zamborini, F. P., Murray, R. W. (2004) Growth, conductivity and vapor response properties of metal ion-carboxylate linked nanoparticle films, *Faraday Discuss.*,125, 63-76.
3. Zamborini, F. P., Leopold, M. C., Hicks, J. F., Kulesza, P. J., Malik, M. A., Murray, R. W. (2002) Electron hopping conductivity and vapor sensing properties of flexible network polymer films of metal nanoparticles, *J. Am. Chem. Soc.*, 124, 8958-8964.
4. Brust, M., Walker, M., Bethell, D., Schiffrin, D. J., Whyman, R. (1994) Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid-liquid system, *J. Chem. Soc. Chem. Commun.*, 801-802.

Effect of scattering loss on optimized waveguide enhanced Raman spectroscopy sensors

Zhen Liu[1], Mohamed A. Ettabib[1], James S. Wilkinson[1], Michalis N. Zervas[1,*]
[1] Zepler Institute for Photonics and Nanoelectronics, University of Southampton, Southampton SO17 1BJ, UK

Abstract:
The strong evanescent field at the interface of a waveguide is utilized in waveguide enhanced Raman spectroscopy (WERS) for high sensitivity sensing. WERS signal collection efficiency is usually maximized by optimizing the waveguide parameters to maximize a (conventional) figure-of-merit (FOM) expressed as the product of the pump and signal surface modal-field-squared [1]. Waveguide signal collection is also known to be dependent on the waveguide length and propagation loss, which is usually considered as a constant. However, propagation loss is dominated by surface scattering, which is known to vary with the waveguide parameters [2], as shown in Fig. 1. It is observed that the waveguide thicknesses that maximize the surface field-squared and the scattering loss do not in general coincide and this is expected to affect the overall WERS optimization.

In this work, we introduce a new FOM, in which in addition to the pump and signal surface modal-field-squared, we consider the scattering loss dependence on waveguide parameters. Slab waveguides with Ta_2O_5 core, SiO_2 substrate and water superstrate are studied at a wavelength of 785nm, and a surface roughness of 1nm RMS was assumed. Figure 2 plots the new FOM as a function of the waveguide core thickness and sensing length. It is found that the thickness of the waveguide that maximizes the surface modal field squared alone (conventional FOM) does not maximize the new FOM because of the interplay with the scattering loss and its dependence on the waveguide parameters. Specifically, while the conventional approach results in an optimized core thickness of 81nm, the new approach results in an optimum of 117nm and an increase in Raman signal collection efficiency by a factor of 2.85, despite the reduced surface intensity, because of the reduced scattering loss. This approach is expected to increase substantially the optimized WERS sensor efficiency. Further results for TE and TM single-mode and multi-mode excitation/collection will be presented.

Keywords: waveguide enhanced Raman spectroscopy, scattering loss, slab waveguide, tantalum pentoxide

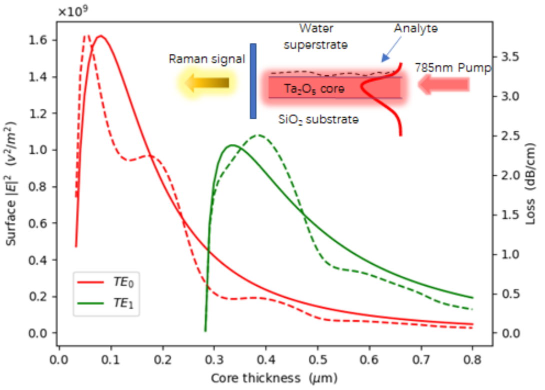


Figure 1. Surface modal field squared (solid lines) of different spatial modes and their corresponding scattering loss (dashed lines) resulting from an assumed RMS roughness of 1nm, as a function of the thickness of the waveguide core. The waveguide is a three-layer slab waveguide with Ta_2O_5 core, SiO_2 substrate and water superstrate.

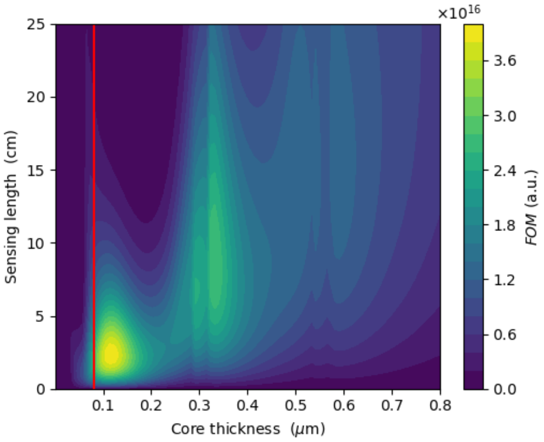


Figure 2. New FOM as a function of waveguide thickness and length for TE_0-pumped Ta_2O_5 slab waveguide based WERS. The red line denotes the thickness that maximizes efficiency on the basis of the surface modal field squared alone.

References:

1. D. M. Kita, J. Michon, S. G. Johnson, and J. Hu. (2018) *Optica*, 5, 9, 1046-1054.
2. J. H. Schmid et al. (2008), *Opt. Lett.*, 33, 13, 1479-1481, doi: 10.1364/ol.33.001479.

Paper-based electrochemical (bio)sensors as novel more sustainable devices

D. Moscone[1*], F. Arduini[1,2]
[1] Department of Chemical Science and Technologies, Tor Vergata University, Rome, Italy,
2 SENSE4MED, Via Renato Rascel 30, 00133, Rome, Italy

Abstract:

In the last decade, paper has been discovered as a powerful tool for developing analytical devices characterized by very interesting features: it is cost-effective, does not require additional components (i.e. pump) for microfluidic handling of the sample, and allow avoiding sample treatment thanks to the filtering property of paper. The first examples of these devices consisted in colorimetric assays; however, immediately after the electroanalysis has discovered the utility of using paper as electrode-active support, joining the reported advantages of paper with the features of electroanalysis, such as high sensitivity, selectivity and capability to work in complex matrices (e.g. coloured samples). Herein, we reported our recent research activity for the development of innovative sensing platforms, exploiting printed-electrochemical sensors also modified with nanomaterials, printed-microfluidic platforms and paper as smart support. Several examples will be illustrated, ranging from bio(sensors) useful for personalized medicine to environmental and food applications, including simple sensors although containing all the reagents necessary for field analysis, up to more complex structures such as origami bio(sensors) capable of measuring multiple analytes with the same device, ending with wearable sensors for measuring metabolites in sweat. These examples show as it is possible to develop easy to handle devices exploiting the lab-on-paper concept, saving costs and time, and being able to carry out decentralized analyses.

Keywords: Electrochemical (bio)sensors, Paper-based (bio)sensors, all-in-one (bio)sensors, origami devices, screen-printed electrodes.

Bioanalytical Applications of Enzyme-Mimicking Inorganic Nanoparticles

V.G. Panferov, I.V. Safenkova, N. A. Byzova, A.V. Zherdev, B.B. Dzantiev
A.N. Bach Institute of Biochemistry, Research Center of Biotechnology of the Russian Academy of Sciences, Leninsky prospect 33, 119071 Moscow, Russia

Abstract:

Nanoparticles possessing enzyme-mimicking activity (nanozymes) are considered prospective replacements of natural enzymes for analytical purposes. Stability at a wide range of conditions, high catalytic activity executed by the total surface area, and simple modification provide nanozyme benefits. We have applied nanozymes as a multifunctional tool for lateral flow immunoassay (LFIA) using them as carriers for antibodies, labels, and catalysts for the enhancement of colorimetric signals. Bimetallic and trimetallic nanozymes were obtained, their catalytic properties and efficiency in LFIA were compared.

Bimetallic (Au@Pt) nanozymes were synthesized by overgrowth of Pt-shell around gold nanoparticles. The effects of Au and Pt precursors’ concentration on particle size (from 20 to 60 nm), morphology (from spherical to hierarchically shaped core@shell structures), and optical properties (absorbance spectra) were studied. Trimetallic (Au@Ag-Pt) nanozymes were synthesized via overgrowth of Ag-shell around gold nanoparticles and subsequent galvanic replacement of Ag with $PtCl_6^{2-}$. The effects of silver layer thickness and $PtCl_6^{2-}$ concentration on the particles’ size (from 20 to 70 nm) and morphology (from spherical to multilayer particles with nanosized gaps), and the optical properties of trimetallic nanozymes were studied.

The specific peroxidase-mimicking activity of nanozymes was within the range of 0.06–13.1 units per mg. The above trimetallic nanozymes facilitated 20–80 times higher activity compared to the bimetallic nanoparticles. Bi- and trimetallic nanozymes maintained peroxidase-mimicking activity in the concentrated hydrogen peroxide (up to 5 M) and elevated temperatures (up to 100 °C). High stability facilitates the specific detection of peroxidase-mimicking activity of nanozymes, even in the background of natural peroxidases in biofluids.

The studied nanozymes were conjugated with antibodies via physical adsorption, and the obtained conjugates were used for LFIA of phytopatogens (*Clavibacter michiganensis*, potato virus X) and inflammatory biomarker (C-reactive protein). We validated the developed LFIA test systems on plant extracts, serum, and whole capillary blood. The reduction of the detection limit (up to 500-fold) was achieved via catalytic oxidation of the substrate (3,3′-diaminobenzidine and hydrogen peroxide) on a test strip. At the same time, the duration of the analysis increased insignificantly (from 15 to 20 min) while maintaining the advantages of LFIAs as a means of rapid diagnostics. As a whole, the obtained data demonstrate the benefits of nanozymes as LFIA labels in comparison with conventional nano-sized labels.

This study was financially supported by the Russian Science Foundation (grant number No 19-14-00370).

Keywords: nanozymes, lateral flow immunoassay, core@shell nanoparticles, inflammatory biomarkers.

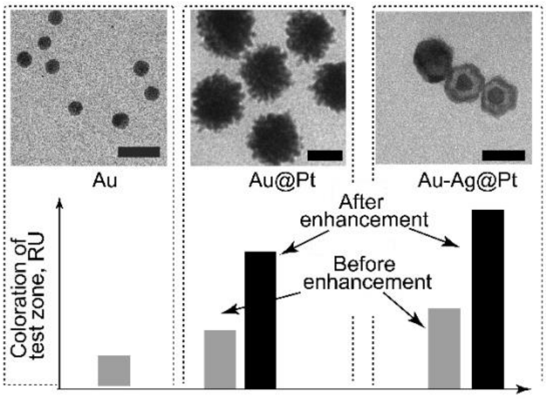


Figure 1:Microphotographs of nanoparticles. Scale bar corresponds to 50 nm. The coloration of the test zone for LFIA using Au, and peroxidase-mimicking Au@Pt and Au@Ag-Pt nanoparticles before and after catalytic enhancement.

Quartz crystal microbalance based sensor for accurate quantification and administration of drug loaded solid lipid nanoparticles for drug release *in-vitro* study

Marco Consumi [1,2*], Luigi Talarico [1,,2], Gemma Leone [1, 2] and Agnese Magnani [1, 2]

1) Department of Biotechnology, Chemistry and Pharmacy, University of Siena; Via Aldo Moro 2, 53100 Siena, Italy;
2) National Interuniversity Consortium of Materials Science and Technology (INSTM) – Siena Research Unit, Via G. Giusti 9, 50121 Firenze, Italy.

Abstract:
The applications of pharmaceutical and medical nanosystems are among the most intensively investigated fields in nanotechnology The study of new drug delivery systems based on nanoparticles requires both a precise and accurate method for dosing encapsuled pharmaceutical or nutraceutical food supplement compounds and an accurate method to administer a well known amount of nanoparticles.

Studies of polymeric drug-loaded nanoparticles highligh difficulties in validating the data from biodistribution studies without an accurate knowledge of particle phisico-chemical properties.

Piezoelectric sensors may represent a quick and reliable weighing system for drug-delivery nanoparticles and could be useful to quantify the amount of nanopraticles deliver.

Our challenge is the development of a new piezoelectric sensor able to quantify the amount of drug-delivery nanoparticles and control their administration during *in-vitro* studies.

As a proof-of-principle, we developed positively charged monolayers on gold-coated quartz crystals of Quartz Crystal Microbalance (QCM). These sensors were able to trap and weight, via electrostatic interactions, anionic-surface charged solid lipid nanoparticles SLNs.

Controlling the pH of the media we were then able to change the sensor surface charge, thus releasing SLNs.

In particular, self assembled monolayers (SAMs) based on different aminothiols were successfully created on the gold surface of 5 MHz quartz crystals and characterized by ToF-SIMS and Grazing Angle Infrared Spectroscopy, that highlighted each step of protocol.The number of amino groups on the surface was quantified via a reversible Shiff base reaction coupled with spectrophotometric determination. Stearic Acid SLNs were synthesized with a coacervation method and loaded with quercetin. Both loaded and unloaded SLNs were characterized by DLS, z potential measurements, FT-IR spectroscopy. The Quercetin loaded SLNs were then analysed in terms of encapsulation efficiency, release profile, and antioxidant properties.

The QCM sensor could be easily integrarìted along a microfluidic device for *in-vitro* study.

Keywords: quartz crystal microbalance QCM; Solid Lipid Nanoparticles; Quercetin; Coacervation; FTIR; ToF-SIMS; Drug delivery; Controlled release;

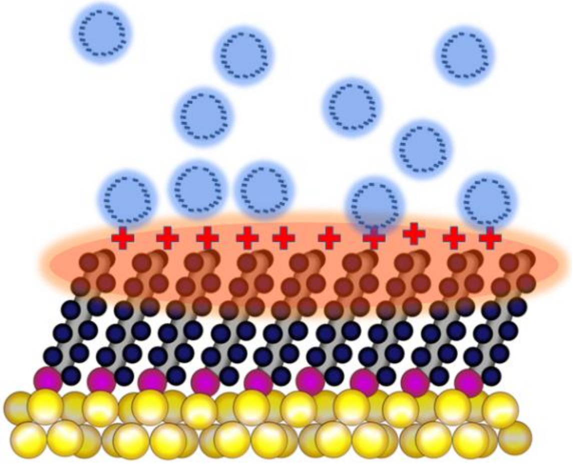


Figure 1: Figure illustrating the Au surface of the QCM sensor (yellow layer) able to trap Solidi lipid nanoparticles (blue spheres) through the positively charged surface (dark blue layer) via electrostatic interaction.

Sensing in Service of Cultural Heritage Protection from Negative Effects of Climate Change

Dr Artur Krukowski and Dr Emmanouela Vogiatzaki
Research for Science, Art and Technology (RFSAT) Limited, Ireland
Artur.Krukowski@rfsat.com and Emmanouela.Vogiatzaki@rfsat.com

Abstract:

The Cultural Heritage plays an important role in defining the identity of Europe as compared to the rest of the World, influencing the feeling of attractiveness for its citizens as a place of work, living and visiting. It increases also the feeling of togetherness among European citizens. Therefore, the need for protecting and preserving European Cultural Heritage is of extreme importance for combined European cultural wealth. The European cultural heritage is enormous, with a vast and rich variety of cultural items, ranging from buildings to museum artefacts. These items consist of materials of diverse types, the condition of which deteriorates with time, mainly due to environmental conditions and human actions. This strengthens the need for the effective documentation of the cultural items, so that information about them is easily accessible to researchers and the public.

The preservation of objects against the effects of time to be passed unaltered to next generations, are also matters of uttermost importance and have attracted significant focus. Factors responsible for the deterioration of the state of cultural items, in case of indoor environments, include but are not limited to, humidity, temperature, exposure to light, as well as the effects of human activities, such as the transportation of the items. These factors are eliminated by keeping the cultural items in specifically designed facilities, such as museums and galleries, where environmental conditions are controlled by following specifications established after extensive research. However, there is a lack of research concerning the effect of the environment and the means to eliminate it, in cases of uncontrolled indoor environments. Such cases include objects and artworks hosted in historical buildings and monuments of public access, where people activities are not restricted, as in museums. The increased human activity, in combination with the uncontrolled environmental conditions of such facilities affects the objects of interest in a significantly higher degree, than the controlled environment of a museum. In this respect, several monitoring and simulation technologies can be effectively used in order to assist in the documentation of cultural objects, as well as the evaluation of the effects of the environment on them and the development of procedures to handle those effects, to achieve preventive conservation.

This article presents an ongoing work in the research project s ARCH, funded by the European Commission under Horizon 2020 program. It concerns means of better preservation of areas of cultural heritage from hazards and risks resulting from Climate Change. It develops tools that will help modern cities to preserve and protect their cultural heritage and historical areas from multiple negative effects of Climate Change. Tools and methodologies are designed for local authorities and practitioners, urban population, as well as national and international expert communities, aiding authorities in knowledge-aware decision making. We will focus attention in our presentation on a variety of sensors and sensing technologies for offering necessary data and beneficial information for being able to produce knowledge-aware decision support tools. Presented approaches range from satellite observations from Copernicus and respective climate and atmospheric monitoring services, through high/low altitude aerial observations to in-situ and mobile sensing at (near) ground levels using novel sensing technologies, some of which have been developed in collaboration with industry leaders such as Analog Devices (Ireland) or Turta (Turkey). Subsequently, application of acquired sensor data in a variety of tools built by other project partners shall be also presented.

Keywords: environmental sensing, pollution sensing, UAS/UAV, cultural heritage, preservation/protection.

Highly fluorescent organic radical nanoparticles as nanothermometer for biological applications

N. Gonzalez-Pato [1,3]*, D. Blasi[1], I. Diez-Zabala[1], S. Srinivasan[1], X. Rodriguez-Rodriguez[1],
J. Guasch[1,2], A. Laromaine[1], J. Veciana[1,3], I. Ratera[1,3]†

[1]Institut of Material Sciecne of Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra, 08193, Spain. [2] Max Planck Partner Group, ICMAB-CSIC, Campus UAB, Bellaterra, 08193, Spain. [3]Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Campus UAB, Bellaterra, 08193, Spain

Abstract:
The appealing optical properties of the tris-(2,4,6-trichlorophenyl)methyl radical (TTM) molecules makes them interesting for their use as fluorescent probes for bioimaging. TTM molecules are considered as inert carbon free-radical for their high chemical and thermal stability, both, in solution and solid state. Its open-shell configuration confer the molecule specific optical characteristics, like emission at large wavelengths, large Stokes shift or emission lifetime of the order of ns[1]. Despite such interesting properties, there are some limiting factors for their use in bioapplications: water compatibility, low fluorescent quantum yield or low photostability. Recently, several molecular approaches have been proposed to enhance these fundamental parameters, highlighting the development of organic nanoparticles (ONPs); these blends are very promising arrangement for fluorescent probes due to its biocompatibility and stability in water. In this work, we report the optical behavior of ONPs made up of blends of the optically neutral tris(2,3,4,5,6-chlorophenyl)methane (TTM-αH), acting as a matrix, doped with the optically active TTM radical. We have demonstrated that TTM radical molecules, shaped like ONPs shows a clear improvement of luminescence and photostability[2]. These ONPs exhibit a dual emission due to radical monomers and excimers at higher wavelenghts. While the monomer emission is almost unaltered varying temperature (internal reference), the excimer emission decrease its intensity while increasing temperature (Figure 1). Moreover, the intensity of these emissions can be modulated with a magnetic field (18 T at 4.2 K) [3] and its excited-state dynamics has been measured using optically detected magnetic resonance (ODMR) corroborating the excimeric emission.[4] These excimers, observed for the first time in the case of a carbon free-radicals, are exploited as nanothermometer for biosensing applications[5], reaching high sensitivity. In order to emonstrate their efficiency for *in-vivo* temperature sensing, we used them to record temperature changes inside *Caenorhabditis elegans* monitoring fluorescence emission, thus demonstrating the biocompatibility and *in-vivo* applicability of the novel nanoparticles.

Keywords: Organic radical nanoparticles, excimer, fluorescence emission, nanothermometer.

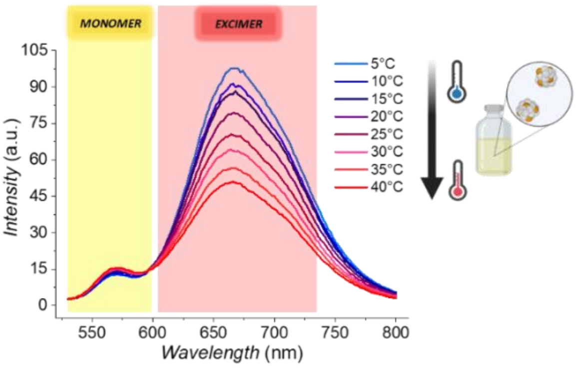


Figure 1: Temperature-dependant fluorescence emission spectra of TTM radical doped ONPs suspended in water.

References:

1. Blasi, D., Nikolaidou, D.M., Terenziani, F., Ratera, I., Veciana, J. (2017), *Phys. Chem. Chem. Phys*., 19, 9313 – 9319.
2. Abdurahman, A., Hele, T.J.H., Gu, Q., Zhang, J., Peng, Q., Zhang, M., Friend, R.H., Li, F., Evan, E.W. (2020), *Nat. Mater.*, 19, 1224–1229
3. Fujiwara, M., Sun, S., Dohms, A., Nishimura, Y., Suto, K., Takezawa, Y., Oshimi, K., Zhao, L., Sadzak, N., Umehara, Y., *et al.* (2020), *Sci. Adv.*, 6
4. Kimura, S., Kusamoto, T., Kimura, S., Kato, K., Teki, Y., Nishihara, H. (2018) *Angew. Chemie - Int. Ed.*, 57, 12711–12715.
5. Kato, K., Kimura, S., Kusamoto, T., Nishihara, H., Teki, Y. (2019) *Angew.*

Chemie - Int. Ed., 58, 2606–2611.

E-mail: * ngonzalez@icmab.es; † iratera@icmab.es

Real-time Thermographic Object Tracking of the Body Temperature of a Neonate

K. Rassels [1], P.J. French [2]
[1] BioMechanical Engineering, TU-Delft, Delft, The Netherlands
[2] Bioelectronics Research Group, TU-Delft, Delft, The Netherlands

Abstract:
Neonates can show sudden rapid body movements when they are in pain, need care, or need to be fed. They can also be very quiet and immovable or move very slowly when they are asleep or being fed.

Monitoring a neonate’s body temperature for a long time provides physicians and caretakers valuable information about the health condition of the baby [1]. Thermographic technology is a remote and very safe way to measure an accurate neonate’s body temperature [2] in order to monitor his/her vital signs. However, the tracking of an elastic thermographic profile of a subject with a random and erratic movement for short- and long-term is a challenging task.

The combination of the real-time thermographic detection and tracking system provides a safe and more robust non-invasive method to measure the vital signs and to monitor the physiological changes of the neonates over time. Tracking of a Thermal Profile Region (TPR) can be achieved by tracking of local Region of Interest (ROI) supported by the global ROI considered as fine and coarse localization and tracking method, respectively. The local tracking is used for very small movements using a reference frame supported by the Optical Flow (OF). However, it is not able to redetect the lost TPR due to the neonate’s displacement (disappearing of ROI from the camera’s Field of View (FOV)) or rapid movement because of the limitations of the OF techniques. ROI results in discarding the related consecutive frames. To solve this problem, long-term object tracking helps to redetect the lost TPR when it reappears in the thermal camera FOV (Figure 1). The feature tracking and triangulation techniques will help to predict the new location of the local ROI and recreate it by overlapping the new ROI with the ROI of the reference frame. If the overlapped region is more than 50% match with the original ROI, it is considered to be the valid recovered local ROI. Otherwise, the lost TPR is not retrievable, and an alarm will be sent to the nurse or physician providing care at that moment.

By tracking and monitoring the vital signs and following the variations and trends of TPR, one can extract valuable features and patterns that can be used in techniques like Artificial Intelligence, Machine Learning, or Deep Learning.

In this paper, a robust real-time model-based single TPR tracking system for neonates is discussed, although, this method can also be used for other target age groups.

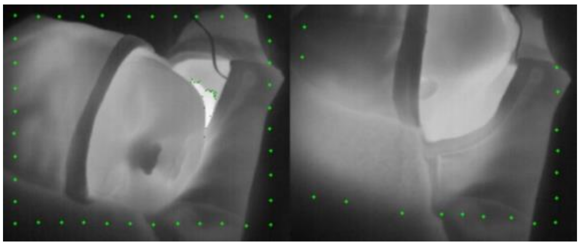


Figure 1: TPR is visible and (re)detected at the left side of the neck which is in the FOV (left picture), TPR is lost because of the baby’s movement (right picture).

Keywords: thermographic object tracking, thermography technology, incubator, infrared thermal imaging, neonates, tracking body temperature, monitoring body temperature, monitoring vital signs, temperature measurement.

References:

1. Darmstadt, G. L., et. al (2004). Topically Applied Sunflower Seed Oil Prevents Invasive Bacterial Infections in Preterm Infants in Egypt. The Pediatric Infectious Disease Journal, 23(8), 719–725. https://doi.org/10.1097/01.inf.0000133047.50836.6f
2. K. Rassels and P. French, “Accurate Body Temperature Measurement of a Neonate Using Thermography Technology,” Smart System Integration (SSI) 2021 (online). doi: 10.1109/SSI52265.2021.9467024

NanoMed 2021 Virtual Session

Gold Nanorods as Theranostic Agent. Applications in Barret Oesophagus, Hepatocarcinoma and Bladder Cancer.

M. Comes Franchini
[1] Department of Industrial Chemistry Toso Montanari, University of Bologna, Italy.
mauro.comesfranchini@unibo.it

Abstract:

It is well known that metal nanoparticles (NPs) have various unusual chemical and physical properties compared with those of metal atoms. The role of organic ligands and their coating is, on the other hand, increasing its importance in nanotechnology and nanomedicine. Once grafted with organic molecules the metallic nanoparticles change their solubility and can therefore be further elaborated and/or entrapped into biopolymers.

Gold nanorods (GNRs), which are tuneable to the near-infrared (NIR) region (800–1100 nm) by manipulation of their aspect ratio (length/width), are particularly attractive agents for theranostic approaches; in particular for diagnosis PhotoAcoustic UltraSound (PAUS) imaging and hyperthermia treatment based on the photothermal effect.

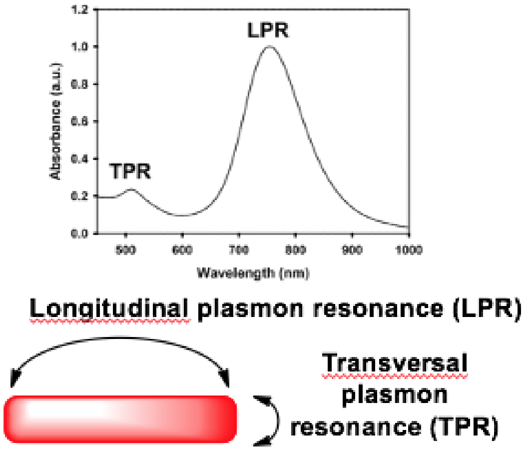


Figure 1: General picture describing the properties of the Gold NanoRods and their Longitudinal and Plasmonic resonance bands.

In the current communication, the coating and/or the polymeric entrapment of GNRs absorbing in the NIR window will be presented. The effective binding capacity of the newly developed nanosystems toward cancer cells was assessed using In Vitro and In Vivo investigation of the death on cancer cell-line and tumor-bearing mice for Barrett Oesophagus, Hepatocarcinoma and Bladder Cancer. The last results on bladder cancer are in the framework of the H2020 funded https://www.edit-h2020.eu. H2020 FETOPEN-2016-2017 (no. 801126, EDIT project 236–238).

Keywords: theranostic, goln nanorods, coating, in vitro, pre-clinical model, Barret oesophagus, Hepatocarcinoma, bladder cancer

References:

1. Current Concepts in Nanostructured Contrast Media Development for In Vivo Photoacoustic Imaging. M. Maturi, E. Locatelli, I. Monaco, M. Comes Franchini. *Biomaterials Science*, **2019**, *7*, 1746-1775.
2. A novel theranostic Gold nanorods- and Adriamycin-loaded Micelle for EpCAM targeting, laser ablation and photoacoustic imaging of cancer stem cells in hepatocellular carcinoma. E. Locatelli, Y. Li, I. Monaco, W. Guo, M. Maturi, L. Menichetti, P. Armanetti, R. C. Martin, M. Comes Franchini *Int. J. Nanomed.* **2019**, *14*, 1877-1892.
3. Gold Nanorods and Curcumin-Loaded Nanomicelles for Efficient in vivo Photothermal Therapy of Barrett Esophagus. **R. C. G. Martin II**,* E. Locatelli, Y. Li, W. Zhang, S. Li, I. Monaco, M. Comes-Franchini. *Nanomedicine*, **2015**, *10*, 1723-1733.

AgNP synthesized by reduction with natural photosensitizer hypericin

R. Rey-Méndez[1*], N. González-Ballesteros[1], F. Fabbri[2], G. Salviati[3], F. Bigi[3,4], M.C. Rodríguez-Argüelles[1]

[1]CINBIO, Departamento de Química Inorgánica, Universidade de Vigo, 36310 Vigo, Spain
[2]NEST, Istituto Nanoscienze-CNR, Scuola Normale Superiore, 56127 Pisa, Italy
[3] CNR-IMEM, 43124 Parma, Italy
[4] Dipartimento Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, 43124 Parma, Italy

Abstract:

Since cancer is still one of the leading causes of mortality in the world, the search for new therapies has drawn much attention. Among them, phothodynamic therapy (PDT) offers outstading advantages from conventional therapies, such as greater efficacy and fewer side-effects. This novel therapy consists in the administration of an organic photosensitizing molecule (PS) followed by irradiation at a specific wavelength, which produces cytotoxic singlet oxygen and/or reactive oxygen species (ROS) inducing cancer cell death. [1]

These PS are usually natural organic molecules, that present several characteristic properties such as non-toxicity in the dark and efficiently generate ROS by irraditation at a specific wavelength. Hypericin (Hyp) is a natural chromophore present in the species of the genus *Hypericum* that has been studied in recent years for its pharmacological properties. Moreover, Hyp is a potent natural photosensitizing agent, that presents no toxicity in the dark, accumulates in tumor tissue preferentialy and efficiently generates ROS and oxygen when irradiated at around 600 nm. Its great potential in photodynamic therapy has been extensively reviewed. [2] Nevertheless, its clinical application presents a major drakback: due to its planar structure, Hyp tends to form aggregates in aqueous environments which limits its solubility and greatly affets its targeting biodistribution. [3] Conjugation of Hyp with metallic nanoparticles can not only overcome these limitations, but also enhance its cytotoxic effect by synergistic photothermal effect. Despite this, the direct synthesis of metallic nanoparticles by reduction with Hyp has not yet been explored.

In this work, the synthesis of silver nanoparticles was achieved by diluting in water 1 mL of a 1 mM solution of Hyp in DMSO, to a final concentration of 0.2 mM. To this solution, 50 µL of a 5 mM $AgNO_3$ solution was added and the mixture was heated to 100ºC with constant stirring. The reaction was followed by UV-Vis spectroscopy and the nanoparticles obtained were characterized by means of transmission electron microscopy (TEM), High Resolution TEM (HRTEM), X-ray diffraction analysis (XRD), energy dispersive X-ray analysis (EDX), Z-potential analysis and Fourier transformed infrared spectroscopy (FTIR). Moreover, *in vitro* biological assays are being performed in order to assess the cytotoxic activity of Hyp@AgNP.

Keywords: PDT, hypericin, AgNP

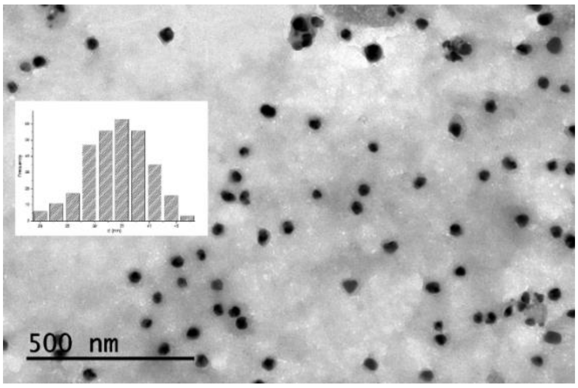


Figure 1: TEM image and the corresponding histogram, showing spherical Hyp@AgNP with an average size of 33 ± 7 nm.

References:

1. Park J, Lee Y, Park I, Hwang SR. Current Limitations and Recent Progress in Nanomedicine for Clinically Available Photodynamic Therapy. *Biomedicines* 9(1) (2021).
2. Jendželovská Z, Jendželovský R, Kuchárová B, Fedoročko P. Hypericin in the light and in the dark: Two sides of the same coin. *Front. Plant Sci.*7, 1-20 (2016).
3. Liu X, Jiang C, Li Y *et al.* Evaluation of Hypericin: Effect of Aggregation on Targeting Biodistribution. *J. Pharm. Sci.* 104(1), 215-222 (2015).

Deformable liposomes loaded into dissolving microneedle array for metastatic melanoma targeting: a preformulation study.

S. Demartis [1,2,*], AJ. Paredes[1], F. Volpe-Zanutto[1], LK. Vora[1], E. Lupinu[2], E. Gavini[2], RF. Donnelly[1]

[1] School of Pharmacy, Queen’s University Belfast, Medical Biology Centre, Belfast, UK
[2] Department of Chemistry and Pharmacy, University of Sassari, Sassari, Italy

Abstract:
Melanoma is one of the deadliest skin cancers for its rapid metastatic ability. Due to biocompatibility and drug delivery efficiency, liposomes were proposed in the literature to treat cutaneous melanoma via dermal delivery [1]. However, the transdermal delivery of a high percentage of intact liposomes must be assured for metastatic cancers. Herein, we combined the delivery strategy of deformable liposomes (transfersomes, TF) with microneedle array patches (MAPs) to study a system to treat metastatic melanoma via transdermal delivery. MAPs can painlessly pierce the outermost layers of the skin and deposit their drug cargo in the dermis. In particular, we report a preformulation study of unloaded TF constituting dissolving MAPs (TF-DMAPs). Two-layered TF-DMAPs were prepared by a two-step casting technique [2] (Figure 1). Two TF dispersions (around 200 nm-sized; PDI<0.3) made of Lipoid S100, cholesterol and Span®80 were used to cast the drug containing layer: TF1 (47.5 mg/mL of lipids) and TF2 (16.88 mg/mL of lipids). One TF-DMAPs (F0) was prepared using 1 mL of TF1 mixed with an aqueous blend (1 mL, 50:50 w/w) of PVA (9-10 KDa) and PVP (58 KDa) 40% w/w; three TF-DMAPs were prepared using 1 mL of TF2 mixed respectively with an aqueous blend (1 mL) of PVA 40% w/w (F1), PVP 40% w/w (F2), and PVA 40% w/w: PVP 40% w/w (50:50 w/w) (F3). The second layer was prepared from an aqueous blend of 30% w/w PVP (90 KDa) and 1.5% w/w glycerol. F0 was discarded as the high lipid amount hampered the microneedles formation; F1-F3 revealed sharp needles observed by light microscope and SEM. F1-F3 mechanical properties (resistance to the compression, Parafilm® insertion test) [2] were studied; the evaluation of the ability of TF-DMAPs to pierce the Parafilm® layers and neonatal porcine skin via optical coherence tomography will be performed. F1-F3 proved to efficiently penetrate two of the eight layers of Parafilm® (252 µm) when submitted to the insertion study [3]; F1 showed a reduction in microneedles length below 3%, F2 and F3 reduction was below 15%. After F1-F3 dissolution, TF2 were still monodispersed (PDI<0.3) and below 250 nm-sized. Considering the promising outcomes, we conclude that F1, F2 and F3 can be selected to be loaded with an anti-melanoma agent and further investigated.

Keywords: liposome; nanoparticle; microneedles; melanoma; transdermal delivery; drug delivery.

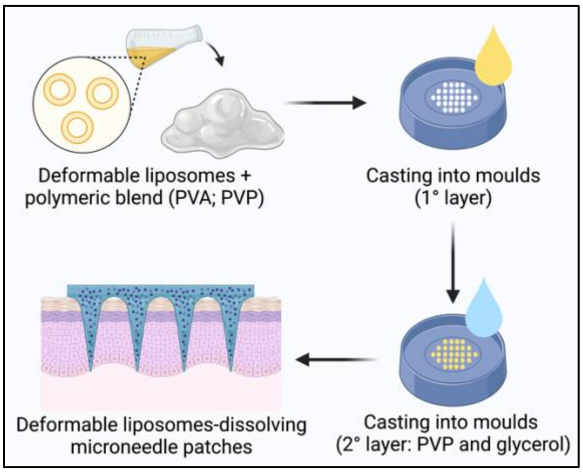


Figure 1. Schematic and simplified representation of deformable liposomes loaded dissolving microneedle patches preparation.

References:

1. Chen Y, Wu Q, Zhang Z, Yuan L, Liu X, Zhou L. Preparation of Curcumin-Loaded Liposomes and Evaluation of Their Skin Permeation and Pharmacodynamics. Molecules 2012;17:5972–87. https://doi.org/10.3390/molecules17055972.
2. Permana AD, Anjani QK, Sartini, Utomo E, Volpe-Zanutto F, Paredes AJ, et al. Selective delivery of silver nanoparticles for improved treatment of biofilm skin infection using bacteria-responsive microparticles loaded into dissolving microneedles. Materials Science and Engineering: C 2021;120:111786. https://doi.org/10.1016/j.msec.2020.111786.
3. Larrañeta E, Moore J, Vicente-Pérez EM, González-Vázquez P, Lutton R, Woolfson AD, et al. A proposed model membrane and test method for microneedle insertion studies. International Journal of Pharmaceutics 2014;472:65–73. https://doi.org/10.1016/j.ijpharm.2014.05.042.

Ultra Magnetic Liposomes : a Versatile Tool for Cancer Therapy

C. Thebault [1,2], A. Michel [1], J. Seguin [2] , N. Mignet [2], B.-T Doan [2], C. Ménager [1]
[1] Sorbonne Université, Laboratoire PHENIX, CNRS, Paris, France
[2] Université de Paris, UTCBS, CNRS, Paris, France

Abstract:

Beyond the properties inherent in liposomes (non-toxicity, in vivo stability, drug encapsulation), ultramagnetic liposomes have remarkable physical properties due to their very high loading in magnetic nanoparticles. They are very good contrast agent in MRI, upon alternative magnetic field they deliver heat (magnetic hyperthermia) and they can be stabilized in tissues with a simple magnet.

Ultra magnetic liposomes were synthesized by reverse phase evaporation (emulsion process) that allows a very good encapsulation of magnetic nanoparticles in their core. The bilayer composition is adjusted in order to be thermosensitive with a transition temperature at 42°C.

We present two different applications of ultramagnetic liposomes for cancer therapy. The first system enables total tumor regression by coupling PDT with magnetic hyperthermia. After intratumoral injection laser or/and magnetic field were applied. A very interesting synergistic effect is observed when PDT is applied before magnetic hyperthermia.

In the second strategy, we propose to design thermosensitive drug-loaded ultra magnetic liposomes to treat superficial colon tumors CT26 on mice. The nanocarriers are accumulated in the tumor by using a magnetic field gradient and the drug release is triggered by a local heating induced by HIFU (High Intensity Focused Ultrasounds). In vivo UML biodistribution was evaluated with dynamic susceptibility contrast imaging in MRI and the accumulation of UML into the tumor after i.v. injection was measured using MRI image percentile processing, iron titration by ICP AES and histology. Co-encapsulation of magnetic nanoparticles and the antitumoral drug CA4P (Combretastatin A-4 Phosphate) provides theranostic properties to our thermosensitive UML. In vitro HIFU heating at the UML membrane transition temperature had shown a 2-fold increase of drug release. Development of in vivo HIFU sequences was performed under MRI thermometry to locally heat the tumor at the transition temperature of the UML membrane allowing to trigger the drug release (Figure 1). As CA4P is a vascular disrupting agent, treatment efficiency is monitored by MRI with perfusion, diffusion and tumor volume regression parameters and by

histology with vascularization and necrosis evaluation.Application of HIFU can, then, be used in the tumor for an active release of the drug in the region of interest for the development of an innovative therapy.

Keywords: magnetic liposomes, cancer therapy, drug release, HIFU

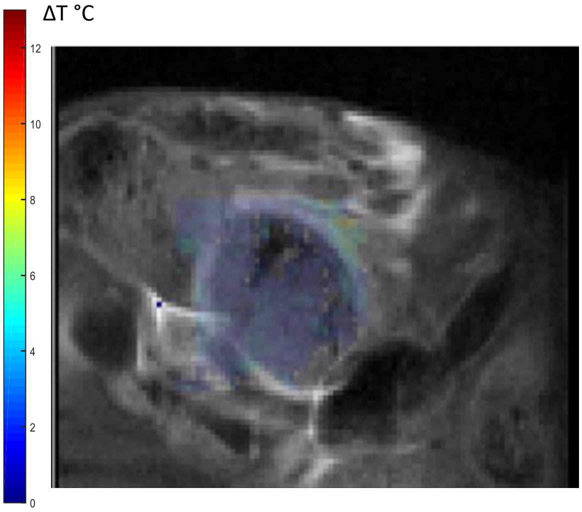


Figure 1: HIFU sequences was performed under MRI thermometry to locally heat the tumor

References:

1. Thebault, Caroline J.; Ramniceanu, Gregory; Boumati, Sarah; Michel, Aude; Seguin, Johanne; Larrat, Benoit; Mignet, Nathalie; Ménager, Christine; Bich-Thuy Doan, Theranostic MRI liposomes for magnetic targeting and ultrasound triggered release of the antivascular CA4P, *Journal of Controlled Release*, 2020, 322, 137-148

2. Thebault, C., Ramniceanu, G., Michel, A., Beauvineau, C., Girard, Seguin, J., Mignet, N., Ménager, C., Doan, B.-T. In Vivo Evaluation of Magnetic Targeting in Mice Colon Tumors with Ultra-Magnetic Liposomes Monitored by MRI. *Molecular imaging and biology*, 2019, 21, 2, 269-278

RNA Gene Medicines: Evolution of Synthetic Carriers

E. Wagner [1,2]
[1] Pharmaceutical Biotechnology, LMU, Munich, Germany
[2] Center for Nanoscience (CeNS), LMU, Munich, Germany

Abstract:

It took fifty years from first RNA transfections to approved gene therapies as drugs [1, 2]. At least eleven gene therapy products, four siRNAs, and more than ten oligonucleotides reached the medical market. Targeted intracellular delivery remains the key requirement for such agents. For this purpose, different chemical evolution approaches are pursued for refinements of synthetic nanocarriers [3]. Natural evolution optimized viruses based on variation and selection of their gene and protein sequences. Our strategy focuses on such a bioinspired, sequence-defined process including (i) artificial amino acids (ii) precise assembly into sequences by solid phase-assisted synthesis (iii) screening for delivery and selection of top candidates, followed by further variation. The optimal sequence of nanocarriers may depend on the cargo, as outlined for pDNA, siRNA [4], Cas9/sgRNA [5], or mRNA [6]. As presented in the first part, optimizing targeted siRNA delivery for knocking down genes in tumors revealed surprisingly different activity in vitro and in vivo, suggesting alternative mechanisms of targeting [7]. Optimizing delivery for Cas9/sgRNA RNPs or mRNA is reported in the second part.

Keywords: gene transfer, gene silencing, genome editing, mRNA, pDNA, siRNA.

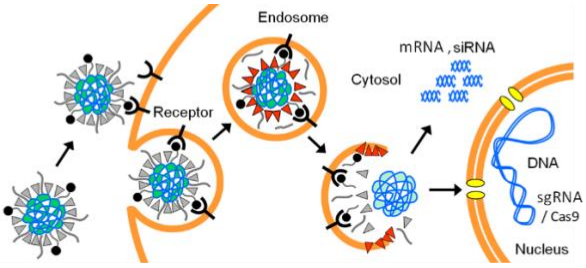


Figure 1: Synthetic nanocarriers need to first compact therapeutic nucleic acids into nanoparticles for protected delivery to the surface of target cells, where receptor-targeted uptake into endosomes and triggered release are required for delivery of mRNA or siRNA into the cytosol, and delivery into the cell nucleus required for function of pDNA or CRISPR Cas9/sgRNA.

References:

1. Vaheri A, Pagano JS (1965) Infectious poliovirus RNA: a sensitive method of assay. *Virology* 27, 434.
2. Lächelt U, Wagner E (2015) Nucleic Acid Therapeutics Using Polyplexes – A Journey of 50 Years (and Beyond). *Chem. Rev.* 115, 11043.
3. Freitag F, Wagner E (2021) Optimizing synthetic nucleic acid and protein nanocarriers: the chemical evolution approach. *Adv. Drug Del. Rev.* 168, 30.
4. Klein PM et al (2018) Folate receptor-directed orthogonal click-functionalization of siRNA lipopolyplexes for tumor cell killing in vivo. *Biomaterials* 178, 630.
5. Kuhn J et al (2020) Delivery of Cas9/sgRNA ribonucleoprotein complexes via hydroxystearyl oligoamino amides. *Bioconjug. Chem.* 31, 729.
6. Krhac-Levacic et al (2021) mRNA lipopolyplexes benefiting from precise redox-sensitive cleavage sites. *J. Control. Release*, in press.
7. Luo J et al (2021) Hyaluronate siRNA nanoparticles with positive charge display rapid attachment to tumor endothelium and penetration into tumors. *J. Control. Release* 329, 919.

Hybrid nanomaterials for biomedical imaging

G. Tobias
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), 08193 Bellaterra, Spain

Abstract:
Carbon nanotubes have been advocated as promising agents for in vivo imaging, tumour targeting and drug delivery systems. When carbon nanotubes are combined with inorganic compounds, the resulting hybrid materials benefit not only from the properties of their constituent nanomaterials but also from synergistic effects. The most explored approach consists on the external decoration of carbon nanotubes with inorganic nanoparticles. One advantage of using carbon nanotubes though is that their inner cavity can be employed for the encapsulation of a chosen payload. The outer surface remains available and can be subsequently modified to attach biomolecules with the aim of improving the dispersability and biocompatibility of the developed hybrids. Even for targeting agents can be anchored to the external surface. In this talk we will see some examples on both the external decoration of carbon nanotubes with inorganic nanoparticles and the encapsulation of a variety of inorganic payloads. The resulting hybrid materials find application in biomedical imaging and are being explored as therapeutic agents.

Keywords: filled cabon nanotubes, carbon nanocapsules, radioimaging, radiotherapy.

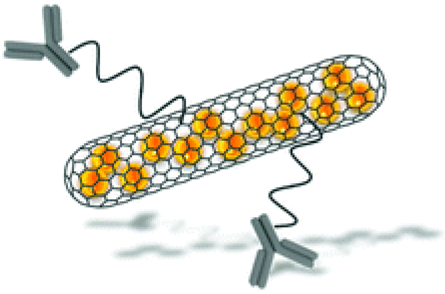


Figure 1: Schematic representation of a filled and functionalized carbon nanotube.

References:
1. J. T.-W. Wang, R. Klippstein, M. Martincic, E. Pach, R. Feldman, M. Šefl, Y. Michel, D. Asker, J. K. Sosabowski, M. Kalbac, T. Da Ros, C. Ménard-Moyon, A. Bianco, I. Kyriakou, D. Emfietzoglou, J.-C. Saccavini, B. Ballesteros, K.T. Al-Jamal, G. Tobias, 2020, ACS Nano 2020, 14,129-141
2. J. T.-W. Wang, C. Spinato, R. Klippstein, P.M. Costa, M. Martincic, E. Pach, A. Perez Ruiz de Garibay, C. Menard-Moyon, R. Feldman, Y. Michel, M. Sefl, I. Kyriakou, D. Emfietzoglou, J.-.C. Saccavini, B. Ballesteros, G. Tobias, A. Bianco, K. T. Al-Jamal, Carbon 2020, 162, 410-422.
3. C.J. Serpell, R.N. Rutte, k. Geraki, E. Pach, M. Martincic, M. Kierkowicz, S. De Munari, K. Wals, R. Raj, B. Ballesteros, G. Tobias, D.C. Anthony, B. G. Davis, Nat.Commun. 2016, 7, 13118.
4. C. Spinato, A. Perez Ruiz de Garibay, M. Kierkowicz, E. Pach, M. Martincic, R. Klippstein, M. Bourgognon, J. Tzu-Wen Wang, C. Ménard-Moyon, K. T. Al-Jamal, B. Ballesteros, G. Tobias, A. Bianco, Nanoscale 2016, 8, 12626-12638.

“Quantum water” in nanoparticulate systems which has a great influence on membrane penetration

I.T. Degim

Departmenmt of Pharmaceutical Technology, Faculty of Pharmacy, Biruni University,
Istanbul, Turkey

Abstract:

Nanotechnology has been vastly used for the development or designing of new and promising drug delivery systems and generally scientist or formulation developers have been mainly focused on nanoparticulate drug delivery system and the physical form and size of the drug particles, but the alteration of water molecules properties in the nanoparticle containing formulation or configuration of water molecules in these formulations has not been properly addressed yet. Quite strange and unexpected experimental results have reported with nanoparticles or nanotubes when they were subjected to the diffusion or penetration experiments[1-3]. It may be possible to alter water properties in these nanoparticulate systems without aiming and without notice. Nanoparticles generally surrounded by water molecules or sometimes water molecules can travel inside of nanotubes. They are then squeezed among or inside of them. It forms an unexpected and entirely new type of molecule; this state of water is called “Quantum water”[4]. The altered dissolving ability of this water can result in alteration of dissolution characteristics of the solution[4]. These may affect permeability, absorption, or bioavailability. All these alterations should be considered before introducing any nanoparticulate/drug system to the market for human use.

Some of our experimental results is going to be presented. These results will be discussed with literature findings. Unexpected results and some new interpretations considering possible consequences, and reasons will be given. This new horizon can open a new window and new requirements can be determined when nanoparticles are going to be used for humans. All these can give better clues for the researcher to explain what is happening in the nano environment in drug formulations with nanoparticles.

Keywords: Nanoparticles, skin penetration, quantum water, penetration enhancement.

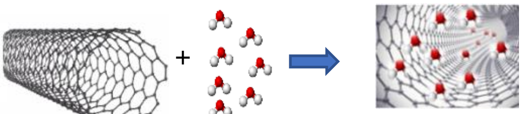


Figure 1: Travel of water molecules to inside of nanotubes.

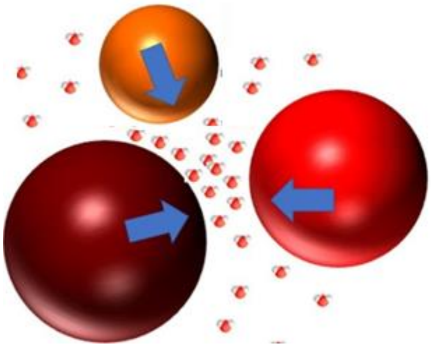


Figure 2: Squeezing or confinement of water molecules among nanoparticles

References:

1. Degim I.T., Burgess D.J., Papadimitrakopoulos, F. (2010) Carbon nanotubes for transdermal drug delivery, *J. Microencapsul*. 27 (8) 669–681.
2. Ilbasmis Tamer S., Degim I.T. (2012) A feasible way to use carbon nanotubes to deliver drug molecules: transdermal application, *Expet Opin. Drug Deliv*. 9 (8) 991–999.
3. Degim I.T., Kadioglu D., (2013) Cheap, suitable, predictable and manageable nanoparticles for drug delivery: quantum dots, *Curr. Drug Deliv*. 10 32–38.
4. Yerlikaya F., Camlik G., Küpeli Akkol E., Degim Z., Degim I., T., Sobarzo-S´anchez E. (2021) Formation of quantum water in nanoparticulate systems, *Journal of Drug Delivery Science and Technology*, 63: 102456. In press.

Temperature-responsive nanogels containing SPIONs and miRNAs for targeted delivery in wound healing and skin regeneration applications. The EuroNanoMed project TENTACLES

Alessandro Paolini[1], Stefania Paola Bruno[1], Arkadijs Sobolevs[2], Aiva Plotniece[2], Marcin K. Chmielewski[3], Natalia Krówczyńska[3], Ludovic Le Hégarat[4], Kevin Hogeveen[4], Monika Sramkova[5], Alena Gabelova[5] Andrea Caporali[6], Nicolás Cassinelli[7], Beatriz Sanz[7], and Andrea Masotti[1]
[1] Bambino Gesù Children's Hospital-IRCCS, Research Laboratories, V.le di San Paolo 15, 00146 Rome, Italy.
[2] Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga LV-1006, Latvia.
[3] FutureSynthesis. Sp. z o.o, Ul. Rubież 46 H, Poznań 61-612, Poland.
[4] Agence nationale de sécurité sanitaire de l’alimentation, del’environnement et du travail, 10 B rue C. Bourgelat, Fougeres 35306, France.
[5] Cancer Research Institute, Biomedical Research Center, Dubravska cesta 9, Bratislava 845 05, Slovakia
[6] University/BHF Centre for Cardiovascular Science, The Queen’s Medical Research Institute, 47 Little France Crescent, EH16 4TJ, Edinburgh, United Kingdom
[7] nB nanoscale Biomagnetics SL, Calle Alaún 14 - nave 7 – 50197 Zaragoza, Spain

Abstract:

Despite recent clinical advances in wound healing, especially on novel materials able to protect the wound and promote healing at the same time, several systemic and local factors can disrupt the physiologic healing process. Therefore, the development of novel therapeutically active wound dressings which provide the wound protection from ‘environmental’ effects as well as wound healing promotion has an advantageous potential for clinical applications [1]. Nanotechnology as a rapidly expanding multidisciplinary scientific field opens the door to innovative therapeutical approaches in the skin repair process. Nanotechnology-based materials incorporated into scaffolds allow the creation of nanocomposite smart materials with unique physicochemical and biological properties promoting skin regeneration. The aim of the TENTACLES project is to develop an innovative multifunctional nanogel that brilliantly integrates the protective (polymer-based nanohydrogel) and healing functions (iron oxide nanoparticles and targeted miRNA) within one nanocomposite smart structure. The heating-mediated stress stimuli via magnetic iron oxide nanoparticles mild fluid hyperthermia (MFH) promote heat shock protein (HSP) induction involved in fibrogenesis [2], extracellular matrix (ECM) production and transforming growth factor-β1 (TGF-β1) activation [3, 4], which is essential to fibrosis. Additionally, miRNA molecules, the key players in the wound repair and regeneration processes [5], contribute to the promotion of the wound healing process via expression modulation of particular genes. The proposed innovative nanocomposite smart nanohydrogel provides revolutionized wound healing therapeutical strategy particularly for diabetic or long stay recovered patients. No evidence has been reported so far about the use of mild hyperthermia and miRNAs in the promotion of skin repair and regeneration.

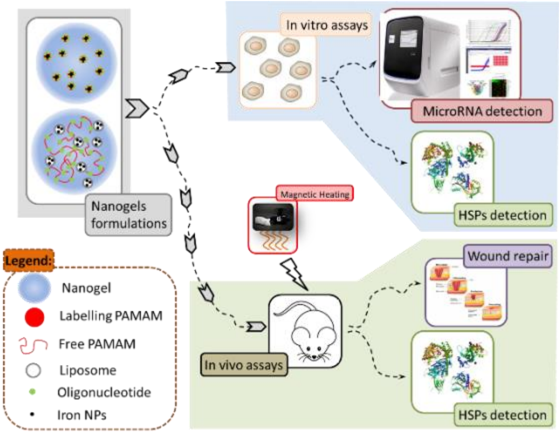


Figure 1: Graphical experimental workflow

To date, many polymeric materials have been clinically used for wound dressing [6], but, actually, none of them contains multiple ‘active’ therapeutic molecules at the same time. Nanogels are polymeric drug delivery systems made by one or more molecules linked together by physical and chemical linkages to form hydrogels [7]. Nanogels, referred also as hydrogel nanoparticles, have the characteristics of both hydrogels and nanoparticles (NPs) [8]. Nanogel drug delivery systems are able to protect effectively active substances from oxidation and degradation [9], therefore macromolecular drugs and therapeutic agents such as siRNA [10-12], DNA [13] and oligonucleotides [14,15] can be stably loaded into these systems. For this purpose, we preliminary prepared and characterized several commercial (Pluronic-F127 and Ca^{2+}-crosslinked alginate), and synthetic biogels (Gelatin-, chitosan- and chondroitin sulphate-methacrylates) containing iron nanoparticles and miRNAs. We analyzed the differences of these biogels and demonstrated their ability to retain the iron oxide NPs within their bulk structure and release miRNAs at the same time. Preliminary results showed the great ability of alginate to entrap both iron oxide nanoparticles and miRNA, and the efficiency of GelMA and pluronic biogels to differently release miRNAs and NPs. Moreover, these hydrogels are also able to heat by electromagnetic irradiation, owing to the presence of iron oxide NPs. These biogels have therefore multifunctional properties and by modulating each of these properties is it possible to create even more complex systems.

In this contribution, we will illustrate the potential application of these biogels, their physico-chemical properties and toxicity profiles on skin models (cells and organoids), and the delivery of selected miRNAs for the modulation of important pathways related to skin regeneration.

Finally, we think that the coupling of different techniques to wound healing, could pave the way to novel industrial opportunities and lead to the realization of patient-oriented devices, aimed at improving the general health status of patients.

Keywords: Nanogel, Wound healing, miRNAs, Heat shock proteins, Iron oxide nanoparticles, Thermal treatment.

References:

1. Kaur IP et al., Curr Pharm Des. 2015;21(12):1556-74.
2. Bellaye PS et al., Pharmacol Ther. 2014 Aug;143(2):119-32.
3. Carew RM et al., Cell Tissue Res. 2012 Jan;347(1):103-16.
4. Klugman J et al., Soc Sci Res. 2012 Sep;41(5):1320-37. Epub 2012 May 11.
5. Liu Y et al., Sci Rep. 2016; 6:32231.
6. Li Y et al., Chem Rev. 2015 Aug 26;115(16):8564-608.
7. Vinogradov SV. Curr Pharm Des. 2006;12(36):4703-12.
8. Hamidi M et al., Adv Drug Deliv Rev. 2008 Dec 14;60(15):1638-49.
9. Kabanov AV et al., Angew Chem Int Ed Engl. 2009;48(30):5418-29.
10. Lee H et al., J Control Release. 2007 Jun 4;119(2):245-52. Epub 2007 Feb 27.
11. Dickerson EB et al., BMC Cancer. 2010 Jan 11;10:10.
12. Kim C et al., Macromolecular research, 2011, 19(2), 166-171.
13. Lemieux P et al., J Drug Target 2000; 8(2):91-105.
14. Vinogradov SV et al., Colloids and Surfaces B: Bio-interfaces, 1999, 16(1), 291-304.
15. Vinogradov SV et al., Bioconjug Chem. 2004 Jan-Feb;15(1):50-60.

Antimicrobial Nanomaterials: will be able to generate Bacterial Resistance?

B.L. España-Sánchez[1*], F.B. Ramírez Montiel[1,2], N.A. Hernández-Santos[1], M.M. Hernández-Orozco[1], F. Padilla-Vaca[2], M.Y. Reyes-Vidal[1], G. Luna-Bárcenas[3]

[1] Centro de Investigación y Desarrollo Tecnológico en Electroquímica CIDETEQ. Parque Tecnológico s/n Sanfandila, Pedro Escobedo Querétaro, C.P. 76703, México.

[2] Departamento de Biología, División de Ciencias Naturales y Exactas, Universidad de Guanajuato. Noria Alta s/n Guanajuato, C.P. 36050, México.

[3] CINVESTAV del IPN Unidad Querétaro. Libramiento Norponiente No. 2000, Fracc. Real de Juriquilla, Querétaro, C.P. 76230, México.

Abstract:

Bacterial resistance has gained important attention due to the its impact on public health. Emerging strategies to avoid the propagation of microorganisms include the use of antimicrobial nanomaterials, such as metallic nanoparticles (NPs) and polymer nanocomposites [1]. Nanomaterials have demonstrated the capacity to inhibit the growth of microorganisms such as bacteria, fungus and virus, and have been considered as the new generation of antimicrobials. In particular, the antibacterial action mechanisms of nanomaterials suggest that the interaction between bacteria/NPs generates simultaneous damage, including the “holes” formation, inhibition of cell wall synthesis and proteins synthesis, oxidative stress by ROS generation and DNA damage [2]. A few reports have been mention that the constant interaction of bacteria with NPs will be generate adaptative bacterial tolerance to NPs micro doses [3]. In this regard, our work describe the early stages of bacterial tolerance analyses to electrospun polymer nanocomposites (polyether sulfone/AgNPs and PCL/CeO_2), based on the consecutive interaction of nanomaterials against *E. Coli* and *S. aureus*, considering the NPs amount and the exposed bacterial concentration. Our results suggest that the antibacterial activity of nanomaterials remains constant after 10 consecutive bacterial expositions, associated with the high antibacterial behavior of electrospun polymer nanocomposites. This study provides preliminar evidence that the use of nanomaterials have potential application as effective antimicrobials.

Keywords: antimicrobial nanomaterials, nanoparticles, polymer nanocomposites, bacterial resistance.

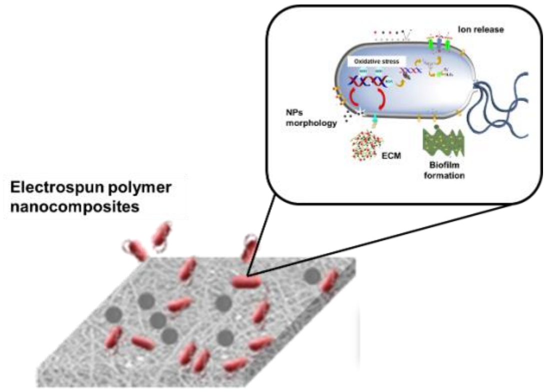


Figure 1: Representative scheme of possible bacterial torerance mechanisms in contact with electrospun polymer nanocomposites.

References:

1. Graves Jr, J.L., Misty, T., Ewunkem, J.A. (2017) Antimicrobial Nanomaterials: Why Evolution Matters?, *Nanomaterials* 7(10), 283.
2. Panacek, A., Kvíter, L., Smékalová, M., Vecerova, R., Kólar, M., Roderová, M., Dycka, P., Sebela, M, Prucek, R., Tomanec, O., Zboril, R. (2018) Bacterial resistance to silver nanoparticles and how to overcome it, *Nature Nanotechnology* 13, 65-71.
3. Niño Martínez, N., Salas Orozco, M.F., Martínez Castañón, G.A., Torres Méndez, A., Ruiz, F., (2019) Molecular Mechanisms of Bacterial Resistance to Metal and Metal Oxide Nanoparticles, *Int. J. Mol. Sci.* 20 (11): 2808.

Nanosystems as enhancements of cell regeneration

A. Minò[1*], G. Testa[2], L. Ambrosone[2]
[1] Department of Biosciences and Territory, University of Molise, Pesche-Isernia, Italy
[2] Department of Medicine and Health Sciences, Univeristy of Molise, Campobasso, Italy

Abstract:

Cardiovascular diseases represent the first cause of morbidity in western countries and, although in the recent years substantial strides have been made in treatment strategies, mortality still remain high. In particular, Chronic Heart Failure (CHF) still remain poor and only few patients access the gold standard treatment, heart transplantation. In the recent decade, medical research has focused its efforts in the attempt of finding new possible strategies for the treatment of CHF. In the last decade, stem cells and the regenerative hypothesis have gained credits especially after the set-up of protocols to reprogram cellular fate to definite phenotypes, suitable for regenerative purposes. First developed for cancer treatment, nanotechnology based approach has opened new perspectives for many fields in medical research, and of course in cardiovascular research [1].

Advances in nanotechnology will provide a tool to efficiently deliver compounds at a defined and sustained rate. Although the exact mechanism of molecular factor activation mediated by small molecules comprising the main regulatory network for a specific cell type remains elusive, a direct reprogramming of mouse fibroblasts into cardiomyocytes with chemical cocktails has recently been successfully performed [2].

In particular, liposomes with dimensions of 100-200 nm have been developed and used as feed reservoirs for fibroblasts. Liposomes are spherical vesicles with an aqueous core entirely enclosed by a lipid bilayer and then they are able to entrap both hydrophilic and hydrophobic chemicals [3] (Figure 1). While liposome capacity to retain hydrophobic molecules depends on the double lipid layer, its internalisation in cells is closely related to surface charge. To improve the fluidity of lipid bilayer and reduce the permeability of hydrophilic molecules cholesterol is used, in appropriate proportions, as component of the liposome. Before being given to fibroblasts, the nanosystems loaded with the chemicals were chemically and physically investigated. The surface charge of liposomes loaded with chemicals was carried out by means of Zeta-potential measurements while the dimensions of the individual systems were monitored with dynamic light scattering.

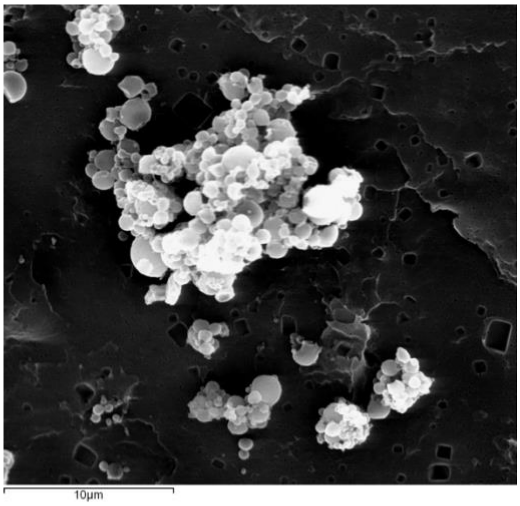


Figure 1: Scanning electron micrographs showing fine-scale surface textures of liposomal dispersion.

Furthermore, the molecular morphology was evaluated by fluorescence and UV-visible absorption spectroscopy. Experimental results have shown that the use of nano-containers increases the transformation yield of mouse embryonic fribroblasts into cardiomyocytes.

Keywords: Regeneration, liposomes, fibroblasts, Zeta-potential, cardiomyocites, mouse embryonic fribroblasts.

References:

1. Passaro, F., Testa, G., Ambrosone, L., Costagliola, C., Tocchetti, C.G., Di Nezza, F., Russo, M., Pirozzi, F., Abete, P., Russo, T., Bonaduce, D. (2017). Nanotechnology-based cardiac targeting and direct cardiac reprogramming: the betrothed. *Stem Cells International*, 2017, Article ID 4940397.
2. Passaro, F., Tocchetti C.G., E., Spinetti, G., Paudice, F., Ambrosone, L., Costagliola, C., Cacciatore, F., Abete, P., Testa, G. (2021). Targeting fibrosis in the failing heart with nanoparticles. *Advanced Drug Delivery Reviews*, 174, 461-481.
3. Di Nezza, F., Zeppa L., Costagliola C., Bufalo G., Ambrosone L. (2019). A physicochemical study of ophthalmological vital dyes: From dimerization equilibrium in buffer solution to their liposomal dispersions. *Dyes and Pigments*, 162, 680-687.

Molecular Dynamic study of antitumoral drug Cisplatin confinement inside edge-functionalized carbon nanotubes and its release near cell membrane

Alia Mejri[1,2], Bahoueddine Tangour[1], Guillaume Herlem[2], and Fabien Picaud[2]
[1] Unité de Recherche de Modélisation en Sciences Fondamentales et Didactiques, Equipe de Chimie Théorique, Université de Tunis El Manar, BP 254, El Manar 2 2096, Tunisia.
[2] Laboratoire de Nanomédecine, Imagerie et Thérapeutiques, EA4662, UFR Sciences et Techniques, Centre Hospitalier Universitaire et Université de Bourgogne Franche Comté, 16 route de Gray, 25030 Besançon, France

Abstract:

Cisplatin drug molecule (CDDP) is widely used in chemotherapy medication for the treatment of various types of cancer. Unfortunately, this molecule is unstable during its administration, causing several side effects, even damaging healthy cells close to those targeted. To overcome the CDDP cytotoxicity, one of the most considered solutions is to confine it into carbon cages such as single walled carbon nanotubes (SWCNTs)[1] before delivering them near their target cells.

Frequently during their synthesis, the CNTs are cutted and functionalized by oxidation process allowing saturation of CNTs dangling bonds with alcohol functions (- OH) for instance.

In the current study, Molecular Dynamics simulations are performed to evaluate the influence of CNTs chemical functions (-H, -OH) on the input/output process and the retention time of CDDP molecules throughout the process of vectorization to a cell membrane[2].

Keywords: CNT, POPC membrane, encapsulation, drug delivery,Cisplatine

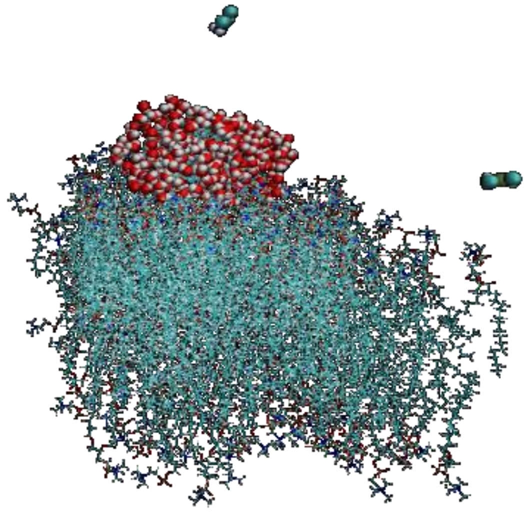


Figure 1: (CNT + CDDP) system near the POPC membrane.

References:

1. A. Mejri, D. Vardanega, B. Tangour, T. Gharbi, F. Picaud, J. Phys. Chem. B **119**, 604 (2015)
2. A. Mejri, B. Tangour, G. Herlem and F. Picaud, *The European Physical Journal D*, **75**, 99, (2021).

Evaluation of cytotoxicity of thiolated organosilica nanoparticles and the effect of PEGylation on toxicity reduction

Balnur A. Zhaisanbayeva[1], Ellina A. Mun[2], Ivan A. Vorobjev[2], Gonzalo Hortelano[2], Vitaliy V. Khutoryanskiy[3]

[1] - School of Engineering and Digital Science, Nazarbayev University, Nur-Sultan, Kazakhstan
[2] - School of Sciences and Humanities, Nazarbayev University, Nur-Sultan, Kazakhstan
[3] - School of Pharmacy, University of Reading, UK

Abstract:

Silica nanoparticles are gaining high interest among inorganic nanoparticles for biomedical applications due to their small size, stable chemical structure and high surface reactivity[1]. Those properties of silica nanoparticles are notional to use in drug/gene delivery, medical imaging and tissue engineering[2]. A variety of methods for the synthesis of silica nanoparticles have been developed and employed. However, the toxicity profile of these nanoparticles is still not clear and the toxicity data of silica nanoparticles are often contradicting.

We evaluated *in vitro* and *in vivo* toxicity profiles of organosilica nanoparticles synthesized from (3-mercaptopropyl)tri-methoxysilane (MPTS) by self-condensation[3] for a potential application in drug and gene delivery. The advantages of using this one-step method of synthesis of organosilica nanoparticles are the constant size (45-50 nm), reproducibility and readily available thiol groups on the surface of nanoparticles. These functional groups enable further nanoparticle modification with various ligands.

The toxicological profiles of thiolated and PEGylated (750 and 5000 Da) organosilica nanoparticles were investigated and the effect of PEGylation on toxicological properties of organosilica nanoparticles was studied. It is known that PEGylation of NPs tends to decrease the toxicity, prolong the circulation time of NPs and augment biostability[4]. The particle uptake efficiency and cytotoxicity on different cell lines (HEK293 and MCF7), the hemolytic properties, as well as *in vivo* inflammatory response and biodistribution of nanoparticles in BALB/c mice were evaluated. Our results show that PEGylated nanoparticles have reduced *in vitro* cellular penetration in MCF7 and HEK293 cell lines compared to thiolated nanoparticles (Figure 1). Moreover, the MTT assay and hemolytic assay showed that thiolated and PEGylated nanoparticles did not induce cytotoxicity, as the viability of cell lines did not drop below 70%, suggesting that these nanoparticles are biocompatible[5].

This study contributes to a deeper understanding of the health and environmental impact of organosilica nanoparticles, which is essential for developing silica nanoparticle-based drug delivery systems, providing an incentive to widen the organosilica nanoparticles application.

Keywords: silica nanoparticles, drug delivery, PEGylation, cytotoxicity, organosilica nanoparticles, one-step synthesis, MTT, nanomedicine

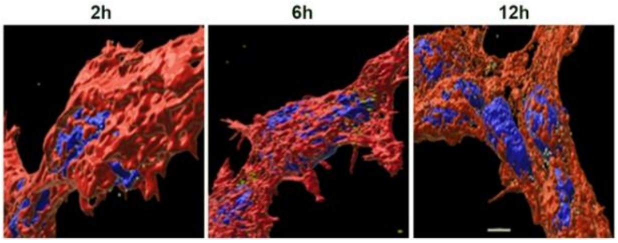


Figure 1: 3D visualization of thiolated nanoparticles' cellular penetration on HEK293 cell line within 12 hours. Stacks of images were taken at 2, 6 and 12 hours of incubation with nanoparticles, by confocal microscopy and processed using IMARIS software. Nuclei are shown in blue, actin in red and nanoparticles in yellow. Scale bar – 4 µm

References:

1. Murugadoss, S. *et al.* (2017), Toxicology of silica nanoparticles: an update, *Archives of Toxicology*, 91, 2967–3010.
2. Wang, D.-P. *et al.* (2020), Silica nanomaterials induce organ injuries by Ca 2+-ROS-initiated disruption of the endothelial barrier and triggering intravascular coagulation, *Part. Fibre Toxicol.*, 17.
3. Irmukhametova, G. S., Mun, G. A. & Khutoryanskiy, V. V. (2011), Thiolated Mucoadhesive and PEGylated Nonmucoadhesive Organosilica Nanoparticles from 3-Mercaptopropyltrimethoxysilane. *Langmuir*, 27, 9551–9556.

4. Fiandra, L. *et al.* (2020), Hazard assessment of polymer-capped CuO and ZnO nanocolloids: A contribution to the safe-by-design implementation of biocidal agents, *NanoImpact*, 17.
5. ISO 10993-5:2009(en), Biological evaluation of medical devices — Part 5: Tests for in vitro cytotoxicity. *Biological evaluation of medical devices* (2009). Available at: https://www.iso.org/obp/ui/#iso:std:iso:10993:-5:ed-3:v1:en. (Accessed: 15th April 2021)

Posters Session

Liquid/aerosol-based atmospheric pressure plasma deposition (APPD) of nanoparticle and metal salt-containing HMDSO coatings

E. Pycha [1,*], S. Chwatal[1], M. Stummer[2], S. Gümüs[3] A. Schwan[1], J. Lackner[1], W. Waldhauser [1]

[1] JOANNEUM RESEARCH Forschungsgesellschaft mbH, MATERIALS - Institute for Surface Technologies and Photonics, Niklasdorf, Austria
[2] INOCON Technologie GmbH, Attnang-Puchheim, Austria
[3] KOCAELI UNIVERSITÄT, Fakultät für Maschinenbau, Metallurgie und Werstofftechnik

Abstract:
Atmospheric pressure chemical vapor deposition (APCVD) generally enables the generation of silicone and silicate based thin films at low costs, resulting in a variety of applications. Previous studies indicate that an extenisve surface functionalization, using hexamethyldisiloxane (HMDSO) precursors, quickly reaches its technical limits. However, a multifluidal driven APCVD process using aerosols and HMDSO precursors, is a promising approach to overcome the technical limits and enables new types of functional nano-coatings. (1)(2)

In this work, nano-layers are deposited on substrates by AAPPD, whereby salt solutions or dispersions of nanoparticles are injected to the plasma plume, achieving corrosion resistant or photocatalytic coating systems. Simultaniously, HMDSO precursors are injected externally, stabilizing the AAPPD process and increases the functionality of the nano-coatings even further, e.g. self-healing, self-cleaning. A series of qualitative and quantitative studies were carried out to investigate the layer generation, the layer morphology depending on different fluids and process conditions. Highly promising for the production of active anti-corrosion coatings is water-dissolved Ce(III)NO_3 salt (3), leading to formation of cerium hydroxide in the coatings. These formed insoluble hydroxide deposits act as a corrosion inhibitor and delays further corrosion reactions by strong volume increase during oxidation. Electrochemical investigations proved that the corrosion resistance increased with increasing cerium content. Additionally, catalytic effects of HMDSO layers with core-shell-TiO_2-anatase-nanoparticles were measured. The optimisation of these catalytic layers is supported by CFD-simulation, investigating local thermo-physical effects to achieve optimal APCVD-parameter settings. (see figure 1).

Keywords: hexamethyldisiloxane (HMDSO) layers, atmospheric pressure chemical vapor deposition (APCVD), aerosol-assisted atmospheric pressure plasma deposition (AAPPD), active corrosion protection, self-cleaning, Ce(III)$NO_{3,}$ core-shell-TiO_2-anatase nanoparticles, catalytic effects.

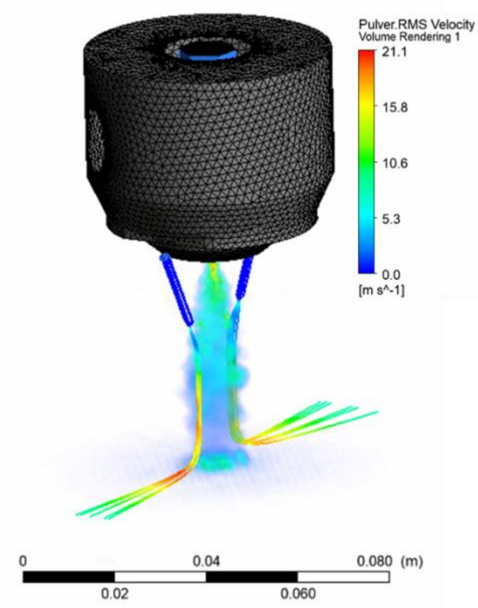


Figure 1: Simulation of spatial RMS-fluid velocity distribution of APCVD using ethanol with dispersed TiO_2 nano-particlesANSYS19.0 R3).

References:

1. Rügner, K., Reuter, R., Ellerweg D., Arcos, T., Keudell, A., Benedikt, J. (2013), Insight into the Reaction Scheme of SiO_2 Film Deposition at Atmospheric Pressure, *Plasma Process. Polym.* 10,1061-1073
2. Palumbo, F., Lo Porto, C., Fracassi, F., Favia, P. (2020), Recent Advancements in the Use of Aerosol-Assisted Atmospheric Pressure Plasma Deposition, *Coatings*, 10, 440
3. Nauman, M., Jin, H. and Shawei, T. (2017), Electrochemical Study of Unmodified and Inhibitor Doped Silane Films for Corrosion Protection of AA2024-T3, *IOP Conf. Ser.: Mater. Sci. Eng.*, 230, 012045

Laser texturing of PET in silver nanoparticle colloids

J. Siegel [1,2,*], J. Pryjmaková [1,2], V. Švorčík

[1] Department of Solid State Engineering, University of Chemistry and Technology Prague, Prague, Czech Republic

Abstract:

Natural and synthetic polymeric materials are widely used in the manufacture of biomedical supplies [1]. Due to the versatility of their surface properties which may easy be tailored by means of physical and chemical processes, polymers are suitable candidates for biomimetic structures in medical applications. These biomaterials are particularly used in tissue engineering, implants, drug delivery carriers, wound healing materials or in biological imaging.

A common problem in current research of polymers for biomedical applications is the adhesion of bacteria and the formation of biofilms on the surface of medical devices. Bacteria cause infections and inflammation. To improve the bactericidal and anti-biofilm properties of biomaterials, various methods of their surface modification have been developed. The most common one is the coating of their surface with antibiotics. However, bacteria succeed in developing mechanisms to neutralize the effect of these therapeutics [2]. According to the World Health Organization, bacterial resistance to antibiotics, which is constantly increasing in all parts of the world, is today one of the greatest threats to health, agriculture and the food industry [3]. In addition, antibiotics have a number of disadvantages, including poor solubility, instability, and side effects. Therefore, alternatives to antibacterial therapy are intensively sought.

We report on a novel technique of surface texturing of polyethyleneterphtalate (PET) foil in the presence of silver nanoparticles (AgNPs). This approach provides a variable surface morphology of PET evenly decorated with AgNPs. Surface texturing occurred in silver nanoparticles colloids of different concentrations under the action of pulse excimer laser. Surface morphology of PET immobilized with AgNPs was observed by AFM and FEGSEM. Atomic concentration of silver was determined by XPS. Presented concentration-controlled procedure of surface texturing of PET in the presence of silver colloids leads to a highly nanoparticle enriched polymer surface with a variable morphology and uniform nanoaprticle distribution.

Keywords: polymer, silver nanoparticles, surface texturing, excimer laser, surface morphology

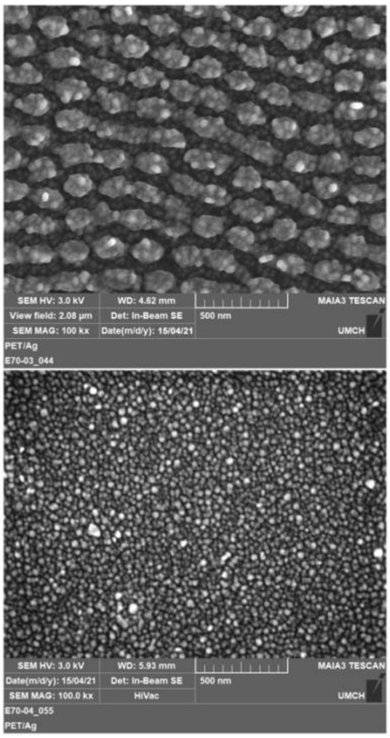


Figure 1: FEGSEM micrographs showing the surface morphology of PET after its irradiation in the presence of AgNPs colloid of different Ag concentrations: (up) 15 mg l^{-1} and (down) 30 mg l^{-1}.

References:

1. Slepicka, P., Siegel, J., Lyutakov, O., Kasalkova, N.S., Kolska, Z., Bacakova, L., Svorcik, V. (2018), Polymer nanostructures for bioapplications induced by laser treatment, *Biotechnol. Adv.*, 36, 839-855.
2. Skarzynska, M., Zajac, M., Wasyl, D. (2020), ANTIBIOTICS AND BACTERIA: MECHANISMS OF ACTION AND RESISTANCE STRATEGIES, *Adv. Microbiol.*, 59, 49-62.
3. Mahase, E. (2020), More countries report on antibiotic resistance but results are "worrying," says WHO, *BMJ Brit. Med. J.*, 369.

Cellulose-based composite aerogel: perspectives for environmental applications

M. Zannotti [1,*], A. Rossi[1] and R. Giovannetti[1]
[1]School of Science and Technology, Chemistry Division, University of Camerino,
62032 Camerino, Italy

Abstract:

Cellulose, the most abundant natural polymer on the planet, offers a great variety of characteristics ranging from excellent biocompatibility to reduced costs. Therefore, this compound is a valid alternative for conventional raw materials.

Aerogel material is a sol-gel material where the liquid component of the gel has been replaced by air, leaving intact the solid structure without collapsing of the material, in which air is at around 90-99% in air by volume [1].

Aerogel prepared using cellulose has the renewability, biocompatibility, and biodegradability of cellulose, with additional advantages, such as low density, high porosity, and a large specific surface area [2].

In this study, an inexpensive sol-gel process, using a green approach, to produce cellulose-based aerogel from recycled cellulose was optimized. Successively, the sol-gel process was modified to produce cellulose-based aerogel doped with graphene in order to improve the performance and enlarge the perspectives of this material. In this case, reduced-graphene oxide was directly synthesized inside the precursor solution during the formation of the aerogel. These cellulose-based aerogel materials were deeply characterized by SEM, IR and Raman spectroscopy and the absorption capacity towards pollutants dyes such as Methylene-Blue and Rhodamine-B in water solution, was studied. Kinetics, equilibrium isotherm and efficiency in the adsorption process were elucidated. The absorption process, for both the undoped and graphene-doped material, follows the Freundlich isotherm model, indicating a multilayer absorption mechanism through chemical-physics absorption. In addition, the kinetics studies demonstrated the higher performance of graphene-doped materials for the absorption of the investigated organic dyes in water solution.

Keywords: aerogel, cellulose, graphene-oxide, absorption, absorption kinetics, equilibrium isotherms

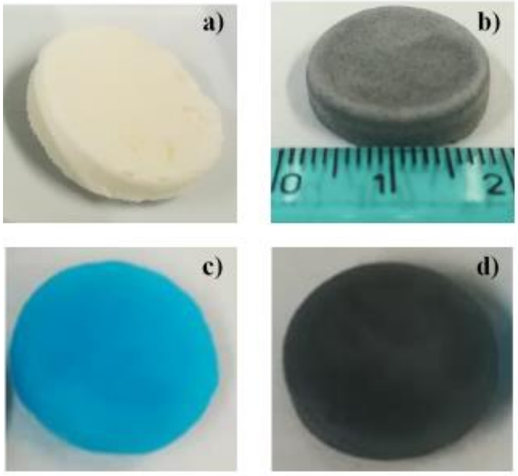


Figure 1: a) Cellulose and b) graphene-doped cellulose aerogel; c) cellulose and d) graphene-doped cellulose aerogel after Methylene-Blue absorption process.

References:

1. Du, A., Zhou, B., Zhang, Z., Shen, J. A (2013) Special Material or a New State of Matter: A Review and Reconsideration of the Aerogel. *Materials*, 6 (3).
2. Long, L.-Y., Weng, Y.-X., Wang, Y.-Z. (2018) Cellulose Aerogels: Synthesis, Applications, and Prospects. *Polymers* , 10 (6).

High Sensitive Ultrathin Flexible Thermoplastic Polyurethane/Carbon Black Fibrous Film Strain Sensor with Adjustable Scaffold Networks

Xin Wang [1], Xianhu Liu [1,2,*], and Dirk W. Schubert [2,3,*]

[1] Institute of Polymer Materials, Friedrich-Alexander-University Erlangen-Nuremberg, Martensstr. 7, 91058, Erlangen, Germany
[2] National Engineering Research Center for Advanced Polymer Processing Technology, Zhengzhou University, 450002, Zhengzhou, China
[3] Bavarian Polymer Institute, Dr. Mack-Strasse 77, 90762, Fürth, Germany

Abstract:
In recently years, high performance wearable strain sensors have attracted great attention in academic and industrial. In this study, a conductive polymer composite of electrospun thermoplastic polyurethane (TPU) fibrous film matrix embedded carbon black (CB) particles with adjustable scaffold network was fabricated for high sensitive strain sensor. This work indicated the influence of stereoscopic scaffold network structure built under various rotating speed of collection device in electrospinning process on the electrical response of TPU/CB strain sensor. This structure makes the sensor exhibited combined characters of high sensitivity under stretching strain (gauge factor of 8962.7 at 155% strain), fast response time (60 ms), outstanding stability and durability (> 10000 cycles) and a widely workable stretching range (0-160%). This high-performance, wearable, flexible strain sensor has a broad vision of application such as intelligent terminals, electrical skins, voice measurement and human motion monitoring. Moreover, a theoretical approach was used to analyze mechanical property and a model based on tunneling theory was modified to describe the relative change of resistance upon the applied strain. Meanwhile, two equations based from this model were first proposed and offered an effective but simple approach to analysis the change of number of conductive paths and distance of adjacent conductive particles.

Keywords: high sensitive strain sensor, electrospinning technology, electronic skin, fitting model

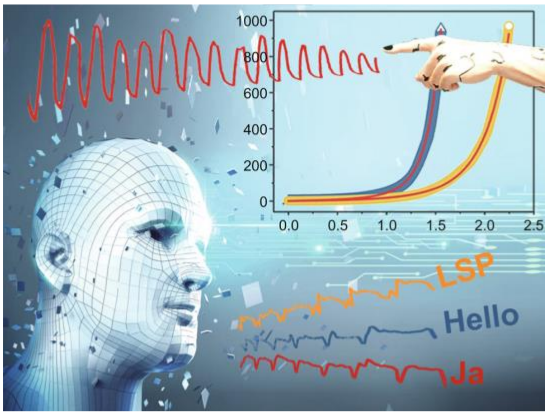


Figure 1: Figure illustrating the body monitoring subtle or large human motions and vocal cord vibration with high sensitive flexible sensor.

References:

1. Wang, X., Liu, X. H. (2021) High Sensitive Ultrathin Flexible Thermoplastic Polyurethane/Carbon Black Fibrous Film Strain Sensor with Adjustable Scaffold Networks. *Nano-Micro. Lett.* 13, 64.
2. Schubert, D. W. (2020) Novel Theoretical Self-Consistent Mean-Field Approach to Describe The Conductivity Of Carbon Fiber - Filled Thermoplastics: Part III—Application of The Concept to Mechanical Properties of Composites and Polymer Solutions. *Adv. Eng. Mater.*, 2000171.

Fast and Green Fabrication of Silica Nanoparticles Coated with Nanosilver as Efficient Antimicrobial Agents

A. Abduraimova[1], T. Mulikova[2], A. Duisembekova[1], A. Molkenova[2], D. Kanayeva[1], T.S. Atabaev[2*]

[1] Nazarbayev University, Department of Biology, Nur-Sultan, Kazakhstan
[2] Nazarbayev University, Department of Chemistry, Nur-Sultan, Kazakhstan

Abstract:

Antibiotic resistance of bacteria is a health threatening issue, which needs to be resolved immediately. In this regard, alternative method for the inhibition of bacterial growth and activity needs to be introduced [1]. Herein, we propose a fast and green method for the fabrication of silica nanoparticles coated with nanosilver (Figure 1). Physicochemical properties of prepared nanocomposite were analyzed by a range of charachterization techniques. Antibacterial activity of prepared nanocomposite was accessed using *E. coli* and *S. aureus* bacterial strains. It was shown that prepared nanocomposite exhibit better antimicrobial activity compared to conventional penicillin antibiotic. The minimum inhibitory concentration as well as the mechanism of inhibition was proposed.

Keywords: silica, nanoparticles, nanosilver, silica-based biomaterials, antimicrobial activity.

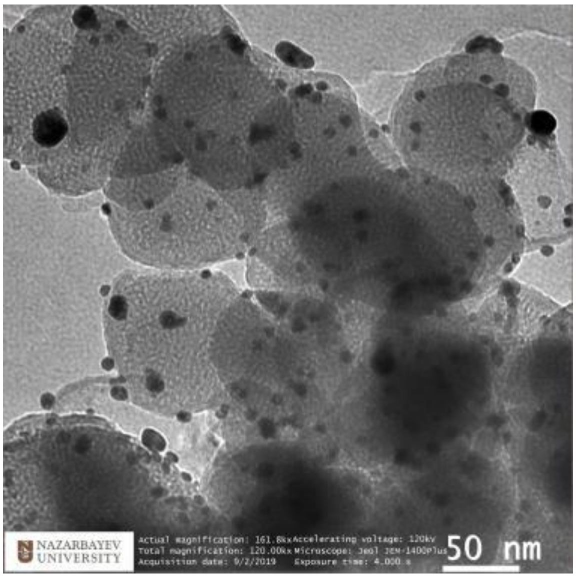


Figure 1: TEM image of silica nanoparticles coated with nanosilver

References:

1. Franci, G. et al./ Silver nanoparticles as potential antibacterial agents, *Molecules* 20 (2015) 8856-8874.

Influence of different types of modifiers on ice adhesion and hydrophobic properties of epoxy resins

G. Morgiante [1], M. Piłkowski [1], J. Marczak [1]
[1] Łukasiewicz Research Network – PORT Polish Center for Technology Development, Wrocław, Poland

Abstract:

Resin surfaces have been widely used in the industry for decades. Their production cost and properties are the most important advantages which determined why they became popular in various branches especially as coatings on materials. Although in cases of hydrophobicity and icephobicity they can not remain their good properties as they are very vulnerable to water and ice. Especially ice accumulation can be troublesome because it can negatively affect the work of power plants, wind turbines causing damages to the structure. The delay in transportation is an another great example how widely this phenomena occurs[1]. Scientists have been trying to solve the problem with many solutions including active electro-thermal heatings systems or the use of freezing point depressant salts or glycol solutions. Modification with fluorinated compounds can solve that problem but solving one creates another which is the presence of toxic fluoric groups in the environment. The research for new products with more eco friendly properties are taken out across the globe[2,3].

In this work, resins have been modified with different types of modifiers: alkyl, fluorinated alkyl and green compounds in order to improve their hydrophobicity. The chemical compositions of obtained coatings were analysed by FTIR. Additionally, thermal stability was investigated using thermogravimetry measurements. Their wettability and later icephobicity were determined on goniometer and specially dedicated apparatus respectively. Obtained results of three different modified epoxy resin coatings have been compared and studied. Presented work provides a concept of promising next step into hydrophobic and icephobic coatings with a chance to be developed further and later applied in the industry.

This work was supported by the National Centre for Research and Development under the LIDER programme through the project contract No. LIDER/47/0194/L-9/17/NCBR/2018.

Keywords: icephobicity, wettability, epoxy resin, epoxy resin coatings, hydrophobicity.

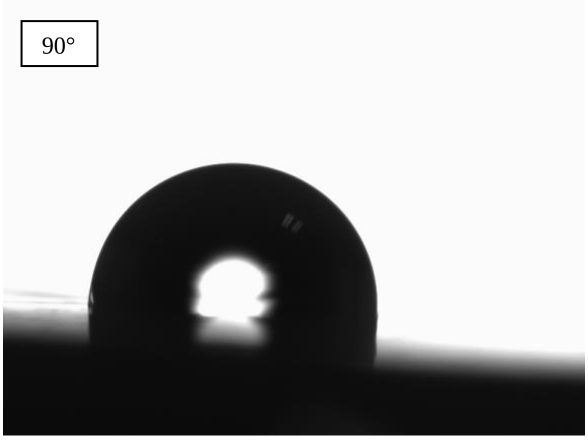


Figure 1: Wettability of epoxy resin sample modified with alkyl modifier.

References:

1. Jamil, M,. Ali, A., Haq, F. eta al. (2018), Icephobic Strategies and Materials with Superwettability: Design Principles and Mechanism, Langmuir, 34, 15425-15444
2. Lyu, J., Wu, B., Wu, N. et al. (2021), Green preparation of transparent superhydrophobic coatings with persistent dynamic impact resistance for outdoor, Chemical Engineering Journal, 404, 126456.
3. Achagri, G., Essamlali, Y., Amedine, O. et al. (2020), Surface modification of highly hydrophobic polyester fabric coated with octadecylamine-functionalized graphene nanosheets, RSC Adv., 10, 24941.

Optimization of the Optical Characteristics of a Multilayer Coating with Thin Films of Germanium Telluride

E. Pritotskii, M. Pankov

Laboratory of neuromorphic optical systems, Institute on Laser and Information Technologies
of Russian Academy of Sciences, Shatura, Moscow region, Russia

Abstract:

Artificial neural networks are implement on elements - synapses with a variable conductivity coefficient [1]. Existing technologies implement synapses based on changes in electrical conductivity in transistors or memristors, however, the criteria for energy efficiency and speed of compute dictate the need for research on optical elements and systems. Optical synapses transmit information using radiation, which propagates along the waveguide. Optical signal is modulated by changing the optical characteristics of the materials used, including laser induction [2]. Energy characteristics of reflection, transmission and absorption of a laser-induced thin film of germanium telluride - GeTe in a multilayer coating are investigated and parameters of a multilayer coating with a four-level transmittance are optimized. The initial data were the optical properties of thin films of GeTe in the amorphous and crystalline states [3]. The wavelength for modulation is 1.55 µm. Refractive index of amorphous film of GeTe is 4, absorption index is 0.1. Refractive index of the crystalline film of GeTe is 6.5, absorption index is 0.7. Refractive index of quartz - SiO2 is 1.46 and refractive index of antireflection coating is 2.4 (such a coating can be zinc selenide - ZnSe). Reflection at the boundaries of thin films can be minimized by using interlayer antireflection coatings (Figure 1), and the achievement of specified transmission levels can be achieved through controlled absorption and determination of the thicknesses of thin films. Calculation model with considering of empirically measured optical properties of phase-changing GeTe under laser-induced action can be interpolated to optical characteristics of a total multilayer coating (Figure 2).

Keywords: optical synapse, neuromorphic system, non-volatile memory, optical properties, optimization of optical characteristics

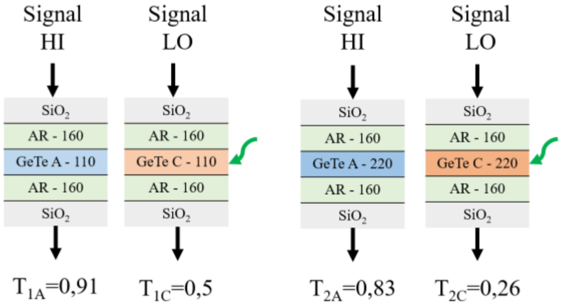


Figure 1: Transmission level for four coatings from left to right: a) 110 nm amorphous film, b) 110 nm crystalline film, c) 220 nm amorphous film, d) 220 nm amorphous film.

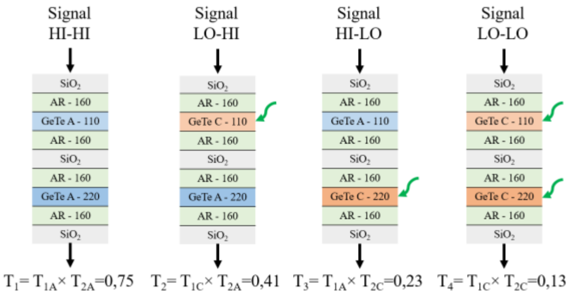


Figure 2: Four levels of transmission with a combination of two coatings from left to right: a) 110 nm and 220 nm amorphous films, b) 110 nm crystalline film and 220 nm amorphous film, c) 110 nm amorphous film and 220 nm crystalline film, d) 110 nm and 220 nm crystalline films.

References:

1. Zhang, W., Mazzarello, R., Wuttig, M., Ma, E. Designing crystallization in phase-change materials for universal memory and neuro-inspired computing. *Nature Reviews Materials.* 4: 150–168 (2019).
2. Gholipour, B., Bastock, P., Craig, C., Khan, K., Hewak, D., Soci, C. Amorphous Metal-Sulphide Microfibers Enable Photonic Synapses for Brain-Like Computing, *Advanced Optical Materials*, 3: 635-641 (2015).
3. Wuttig, M., Bhaskaran, H., Taubner, T. Phase-change materials for non-volatile photonic applications, *Nature Photonics*, 11: 465–476 (2017).

Fluorinated compound as surface free energy lowering agent in hydrophobic coatings

M. Piłkowski [1*], G. Morgiante [1], J. Marczak [1]

[1] Łukasiewicz Research Network – PORT Polish Center for Technology Development, Wrocław, Poland

Abstract:

Surface free energy is one of the key factors in surface wettability, its describes materials affinity to different liquids. Therefore, modifiers that lower surface free energy are crucial for obtaining hydrophobic materials. Commonly such modifiers are used to form thin hydrophobic layers on top of surface, providing desired properties. However, in case of anti-icing systems, those materials lack sustainability after long exposition to external factors. On the other hand, several modifiers can be used for bulk modification of composite coating that can fit into demands of aircraft or energy industry [1]. Our research in this field pushed us towards fluorinated organic compound which work as successful surface free energy agent for epoxy resins. Further research on different epoxy resins brought us to idea of composite coating which hydrophobicity persist even after surface degradation [2].

Characterisation of obtained materials covers wettability tests like WCA (water contac angle) and SFE (surface free energy by van Oss-Good). Moreover obtained resin was measured using FTIR, TG and DSC techniques to ensure synthesis was succsful and to understand its thermal properties [3]. In the end, preliminary tests for ice adhesion properties were performed to ensure that material is suitable for further application testing.

Keywords: surface free energy, wettability, surface modification, composite coating, fluorinated organic compounds.

This work was supported by the National Centre for Research and Development under the LIDER programme through the project contract No. LIDER/47/0194/L-9/17/NCBR/2018.

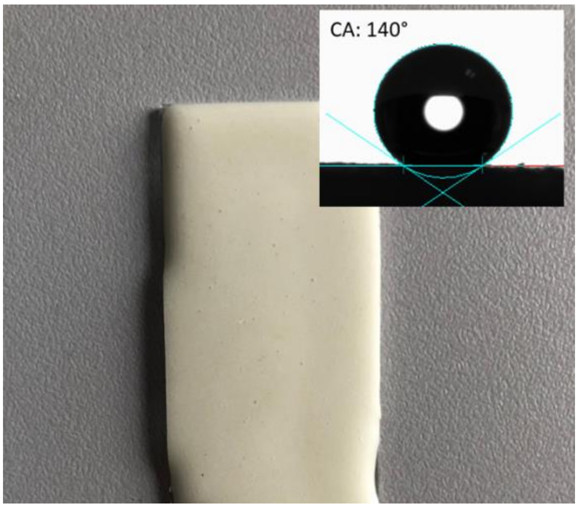


Figure 1: Sample of obtained composite coating with WCA measurement result.

References:

1. Boinovich L.B., Emelyanenko A.M., (2013) Anti-icing potential of superhydrophobic coatings, *Mendeleev Communications*, 23, 3–10.
2. Montoneri F., Montoneri E., Boffa V., Sharts O. (2011), Protein helical structure enhancement in fluorinated-phosphonate nanoporous silica glasses characterized by circular dichroism spectroscopy, *Int. J. Nanotech*., 8, 471-491.
3. Rolere S., Coulon J.F., Poncin-Epaillard F., (2017) Influence of the curing temperature on the diffusion rate of the perfluorinated alkyl chains of a modified epoxy resin, *European Polymer Journal*, 91, 61–69.

Surface Coatings for Small Aircraft Brakes Application

M. Granata[1] and F. Bellucci[1*]

[1]CRdC Tecnologie Scarl, Via Nuova Agnano 11, 80125 Napoli, Italy

Abstract

The rapid development of additive manufacturing technologies has improved the choice of materials in various industrial sectors, specifically relating to friction materials for brakes application in the aeronautical sector. Currently, materials for aircraft brakes range from the low-cost sintered friction pad/liner material vs sintered rotor disc material to the high cost carbon fiber material vs carbon fiber material. The subject of this paper was developed in the framework of a European project (E-BRAKE). One of the objects of this scientific research regards the potential use of thermal spray additive manufacturing technologies to produce a thin film of friction material onto low-carbon steel surface to allow its use as potential composite material for brake units.

In this research friction composite surface coatings were deposited with two different thermal spray additive manufacturing technologies, respectively the High Velocity Oxygen Fuel (HVOF) and the Atmospheric Plasma Spraying (APS), for the purpose of creating high friction and wear resistance composite surface coatings onto low-carbon steel surface. Tribological properties (friction coefficient and wear rate), thermal conductivity, and diffusivity as well as metallographic structures and adhesion to the low-carbon steel surface of these surface coatings were evaluated to assess their potential use as brake materials.

Keywords Additive Manufacturing Technologies · High Velocity Oxygen Fuel · Atmospheric Plasma Spraying · Composite surface coatings · Wear-resistance surface coatings · Friction material coatings

Characterization of materials resulted form spent automotive catalysts using spectrometric techniques

M. Senila [1] *, O. Cadar [1], S. Böringer [2], K. Seaudeau-Pirouley [3], P. Lacroix-Desmazes [4]
[1] INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania
[2] Department Environmental Engineering, Fraunhofer Institute for Chemical Technology ICT, Pfinztal, Germany
[3] Innovation Fluides Supercritiques (IFS), Bâtiment INEED, Alixan, France
[4] ICCM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

Abstract:

Spent automotive catalysts usualy contain important amounts of precious metals, among them Pd and Pt. Natural sources of these metals are generally scarce and, due to their massive industrial utilization, these are highly expensive. Thus, the development of sustainable recycling technologies of precious metals is highly desirable. In order to evaluate the amounts of these elements in used catalysts and to assess the recovery efficiency of the extraction technologies, reliable and precise analytical methods for their determination are required. The direct determination of precious elements in solid catalysts is possible by X-ray fluorescence (XRF), with the main advantage of avoiding sample preparation. However, in the case of quantitative analysis, this technique should be carefully used due to the heterogeneity of the catalyst sample and the flatness of their surface, which can affect the results. Spectrometric methods, such as inductively coupled plasma optical emission spectrometry (ICP-OES) and graphite furnace atomic absorption spectrometry (GFAAS) are powerful tools that can be employed for the determination of Pd and Pt in various sample matrices. However, these methods allow only the injection of liquid samples. In this regard, the digestion of solid sample by microwave-assisted acid extraction procedures at high pressures and temperatures is often used. In this study, a microwave acid digestion method was optimized for the extraction of Pd and Pt from spent catalysts, using a four-step program, at a maximum 200 °C. The resulting solutions were analyzed using ICP-OES, at two different wavelengths for each metal (Pd at 340.458 and 363.470 nm, and Pt at 265.945 and 214.423 nm, respectively) and using GFAAS (Pd at 247.64 nm, Pt at 265.94 nm). Five types of spent catalyst were analyzed and the standard deviations of repeatability for five parallel samples were less than predicted relative standard deviations (PRSD%) calculated using Horvitz's equation for all the analyzed samples.

Keywords: palladium; platinum; ICP-OES; GF AAS, catalysts; method validation; microwave digestion, recycling.

Acknowledgements:

The authors thank CCCDI-UEFISCDI (project number COFUND-ERANET-ERAMIN-SUPERMET, contract 48/2018), JUELICH/BMBF, ADEME, ANR (ANR-17-MIN2-004), for financial support of SUPERMET project (www.supermetproject.eu) in the frame of the ERA-MIN 2 joint call 2017 co-funded by the Horizon 2020 program of the European Union.

References:

1. Senila, M., Cadar, O., Senila, L., Böringer, S., Seaudeau-Pirouley, K., Ruiu, A., Lacroix-Desmazes, P. (2020) Performance parameters of inductively coupled plasma optical emission spectrometry and graphite furnace atomic absorption spectrometry techniques for Pd and Pt determination in automotive catalysts, *Materials*, 13, 5136.
2. Ruiu, A., Bauer-Siebenlist, B., Senila, M., Janisch, T., Foix, D., Seaudeau-Pirouley, K., Lacroix-Desmazes, P. (2020) Promising polymer-assisted extraction of palladium from supported catalysts in supercritical carbon dioxide, *Journal of CO2 Utilization*, 41, 101232.

Bipolar Benzophenone Compounds Bearing Tetrahydrocarbazolyl- and 2-Phenylindolyl- moieties for Application in Optoelectronics

Egle Jatautiene, Rasa Keruckiene, Jonas Keruckas, Ronit Sebastine Bernard, Jurate Simokaitiene, Dmytro Volyniuk, Juozas Vidas Grazulevicius

Department of Polymer Chemistry and Technology, Kaunas University of Technology,
Radvilėnų av. 19, LT-50254 Kaunas, Lithuania

Abstract:
Searching for the new structures of organic compounds as active components of optoelectronic devices remains of great importance in development of efficient organic light emitting diodes and other devices. Molecules possessing properties such as bipolar charge transport, triplet-triplet annihilation, thermally activated delayed fluorescence or aggregation-induced emission enhancement are required.

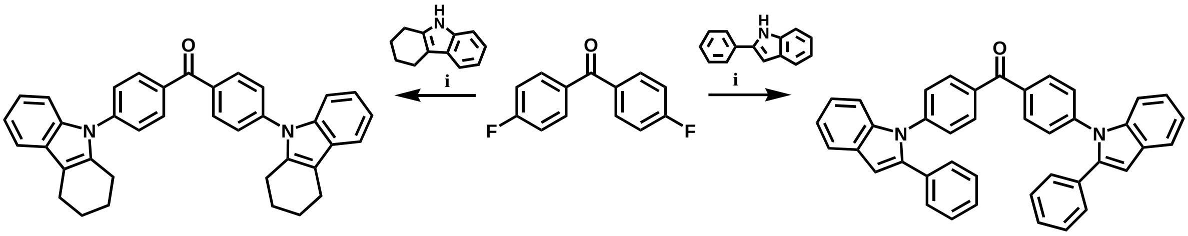


Figure 1: Synthesis of benzophenone derivatives, i) K *t*-BuO, DMSO, R. T., 24 h.

In this work, using donor-acceptor molecular concept, two new electroactive bipolar compounds were synthesized via nucleophilic aromatic substitution reaction, and their thermal, photophysical, electrochemical and photoelectrical properties were tested. Benzophenone was used as an electron accepting moiety, while rarely used tetrahydrocarbazole and 2-phenylindole were used as donor moieties. The yields of the target materials were 66-68 %. Tetrahydrocarbazolyl-substituted benzophenone is capable to form molecular glass with glass transition temperature of 82 ºC. The synthesized compounds showed high thermal stability. The 5% weight loss temperature for tetrahydrocarbazolyl-substituted benzophenone was found to be 447 ºC and in case of 2-phenylindole-substituted derivative it was of 251 ºC. The products exhibited high triplet energy values exceeding 2.8 eV. The ionization potentials estimated by electron photoemission method in air were of 5.54 and 5.53eV. The product with 2-phenylindolyl-moiety exhibited aggregation induced emission enhancement.

Keywords: bipolar, organic light emitting diode, tetrahydrocarbazolyl, phenylindolyl, benzophenone, aggregation induced emission enhancement.

Acknowledgments: this project has received funding from European Regional Development Fund (project No 01.2.2-LMT-K-718-01-0015) under grant agreement with the Research Council of Lithuania (LMTLT).

Mechanochromic luminescent properties of donor-acceptor type organic emitters based on benzanthrone and carbazole moities

Dmytro Volyniuk[1*], Uliana Tsiko,[1] Galyna Sych,[1] Oleksandr Bezvikonnyi,[1] Rasa Keruckiene,[1] Jonas Keruckas,[1] , Ronit Sebastine Bernard,[1] Egle Jatautiene,[1] Algirdas Lazauskas,[2] Juozas Vidas Grazulevicius[1]

[1] Department of Polymer Chemistry and Technology, Kaunas University of Technology, K. Baršausko 59, LT- 51423, Kaunas, Lithuania. *dvolynyuk@gmail.com
[2] Institute of Materials Science, Kaunas University of Technology, K. Baršausko 59, LT-51423, Kaunas, Lithuania

Abstract:

Discovery of organic luminophores with unique properties typically leads to new applications in the field of organic optoelectronics [1, 2]. This work introduces one unique property, i.e. the self-recovering mechanochromic luminescence of the newly synthesized organic semiconductors.

In contrast to many other studies that mainly show effect of crystallisation of organic materials on their mechanochromic luminescence, we demonstrate that mechanochromic luminescence of organic semiconductors is caused by combination of both nano and microscale polymorphs and amorphous aggregates. We also demonstrate the unique potential applications of self-recovering mechanochromic luminescence of the developed compound such as damage-resistive information recording and security probes.

Our molecular design of organic semiconductors with self-recovering mechanochromic luminescence is based on donor-acceptor type molecular structure selecting carbazole and benzanthrone moieties as electron-donating and electron accepting species, respectively. Rigid planar benzanthrone moiety is not yet exploited in the design of organic emitters to the best of our knowledge. The flexibly linked benzanthrone and carbazoles moieties allowed to obtain two smart materials with mechanochromic properties. Analysis of thermally annealed samples by luminescence spectroscopy and single crystal/powder X-ray diffraction analysis revealed multi-color emission of the developed compounds conditioned by the existence of two different polymorphs and aggregates. One compound showed self-reversible mechanochromism and the property of self-recovering (Figure 1). The unique properties of this smart material can be utilized for new security probes or data/code writing with ability to recover after mechanical damage.

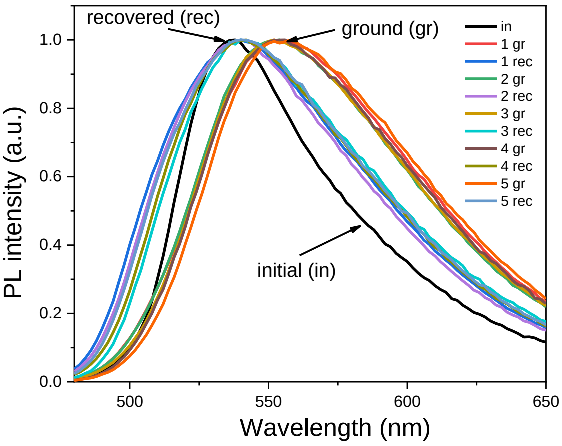


Figure 1: Normalized photoluminescent spectra of one developed compound after five grinding/self-recovery (20 min) cycles.

Keywords: self-recovering, mechanochromic luminescence, benzanthrone, carbazole, information encryption, security check, organic optoelectronics.

Acknowledgements

This project has received funding from European Regional Development Fund (project No 01.2.2-LMT-K-718-01-0015) under grant agreement with the Research Council of Lithuania (LMTLT)

References:

1. W. Yang, Y. Yang, Y. Qiu, X. Cao, Z. Huang, S. Gong, C. Yang, Mater. (2020) IE-active multicolor tunable luminogens: simultaneous mechanochromism and acidochromism with high contrast beyond 100 nm. *Chem. Front.*, **4**, 2047-2053.

Amplification of Pyroelectric Device with WSe_2 Field Effect Transistor and Ferroelectric Gating

S. Mbisike [1,*], J. Phair [2], L. Eckart [2], R. Cheung [1]
[1] Institute for Integrated Micro and Nano Systems, University of Edinburgh, Edinburgh, U.K
[2] Pyreos Limited, Heriot Watt Research Park, Edinburgh, U.K

Abstract:
Since the discovery of infrared (IR) about two centuries ago, IR detectors have found application in medical imaging, military equipment, environmental sensing amongst others. Pyroelectric devices are employed in IR detectors and are finding increased application in IR sensing. Pyroelectricity is the property of certain crystals to spontaneously polarize in response to a change in temperature. The pyroelectric current measured as a result of changes in temperature is dependent on device area and typically in the order of tens of pico-amps. Rencently, Graphene and 2-dimentional (2D) transition metal dichalcogenides (TMD) have been integrated with a pyroelectric device to improve the output signal of the IR detector and performance of the 2D field effect transistor (FET) respectively. In this work, a standalone pyroelectric device (SPD) made from Lead Zirconium Titanate (PZT) with a top and bottom electrode has been fabricated and the pyroelectric current measured with respect to temperature. Also, a 45 nm thick tungsten diselenide (WSe_2) has been exfoliated and deposited onto the thin film PZT allowing for the fabrication of an integrated WSe_2 FET with PZT (IPD). We report signicant difference in the current density measured from the SPD and IPD. The characteristics of the SPD and the IPD as a function of temperature have been analyzed. In addition, the IPD has been gated and the transfer characteristics of the device has been studied. We would discuss the hysteresis behavior observed in the IPD as it relates to control of the WSe_2 FET and also the promise in memory application. Our observation on the IPD further reveals the influence of the gate voltage and temperature change on the polarization experienced within the PZT.

Keywords: WSe_2, PZT, field effect transistor (FET), standalone pyroelectric device (SPD), integrated pyroelectric device (IPD).

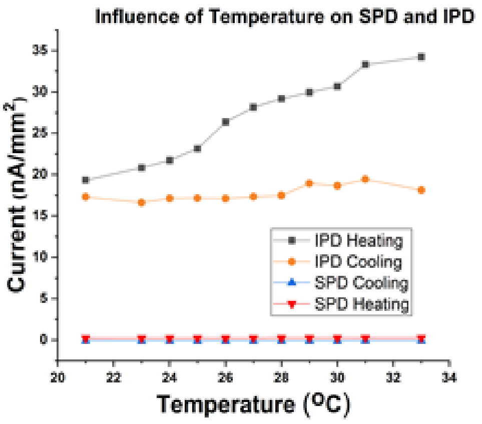


Figure 1: The Figure shows how the current density of WSe_2–PZT FET (IPD) compares to the SPD under the influence of temperature change only.

References:

1. R. Bruchhaus, D. Pitzer, R. Primig, M. Schreiter, and W. Wersing, “Sputtering of PZT thin films for surface micromachined IR-detector arrays,” *Integrated Ferroelectrics*, vol. 25, no. 1–4, pp. 1–11, Sep. 1999, doi: 10.1080/10584589908210154.
2. U. Sassi, R. Parret, S. Nanot, M. Bruna, S. Borini, D. De Fazio, Z. Zhao, E. Lidorikis, F.H.L. Koppens, A. C. Ferrari and A. Colli, “Graphene-based mid-infrared room-temperature pyroelectric bolometers with ultrahigh temperature coefficient of resistance,” *Nature Communications*, vol. 8, p. 14311, Jan. 2017, doi: 10.1038/ncomms14311.
3. X. Zhang, D. Xie, J. Xu, Y. Sun, X. Li, C. Zhang, R. Dai, Y. Zhao, X. Li, X. Li and H. Zhu “MoS_2 Field-Effect Transistors With Lead Zirconate-Titanate Ferroelectric Gating,” *IEEE Electron Device Letters*, vol. 36, no. 8, pp. 784–786, Aug. 2015, doi: 10.1109/LED.2015.2440249

Fabrication of PVDF Porous Structure via Fused Filament Fabrication for Energy Harvesting

Aya Saleh [1*], Garrett W. Melenka [1], Siu Ning Leung [1]
[1] Department of Mechanical Engineering, York University, Toronto, Canada

Abstract:
Smart materials provide great opportunities for energy harvesting through capturing abundant mechanical energy. This work uses fused filament fabrication technique (FFF) to fabricate smart materials for capturing mechanical energy. 3D printing is very promising and opens new possibilities with individualized design for energy harvesters. Porous structures provide many advantages such as lightweight, flexibility, larger deformations under low stress levels, and greater surface area compared to solid designs, which puts forward these structures to boost the mechanical energy harvested. Poly(vinylidene fluoride) (PVDF) is an electroactive polymer with unique electrical properties due to the presence of polar phase (β-phase) in which all dipole moments are arranged in the same direction (all-trans) zigzag conformation.

FFF was used to fabricate porousPVDF structures for energy harvesting. Various printing parameters were studied to investigate their effect on the resultant porous structure in terms of electroactive β-phase formation since its content is crucial for energy genration, mechanical response, and output performance. The printing parameters were filling rate, nozzle speed, and temperature. Afterwards, the obtained structures were characterized using Fourier Transform Infrared (FTIR) technique, Differential Scanning Calorimetry (DSC), and Thermal Gravimetric Analysis (TGA). To better understand and correlate porous structure to the printing parameters, micro-computed tomography (μCT) was performed to assess the resultant pores. In addition to the mechanical characterization performed to evaluate the flexibility of the manufactured porous structures, electrical testing was carried out to quantify the output response.

Keywords: Fused filament fabrication, porous structure, polymers, smart materials, micro-computed tomography, energy harvesting.

References:

1. Qiao, H., Zhang, Y., Huang, Z., Wang, Y., Li, D., & Zhou, H. (2018). 3D printing individualized triboelectric nanogenerator with macro-pattern. *Nano Energy*, *50*, 126-132.
2. Tao, W., & Leu, M. C. (2016, August). Design of lattice structure for additive manufacturing. In *2016 International Symposium on Flexible Automation (ISFA)* (pp. 325-332). IEEE.
3. Kim, D., Park, S. J., Jeon, S. B., Seol, M. L., & Choi, Y. K. (2016). A triboelectric sponge fabricated from a cube sugar template by 3D soft lithography for superhydrophobicity and elasticity. *Advanced Electronic Materials*, *2*(4), 15[illegible]1.

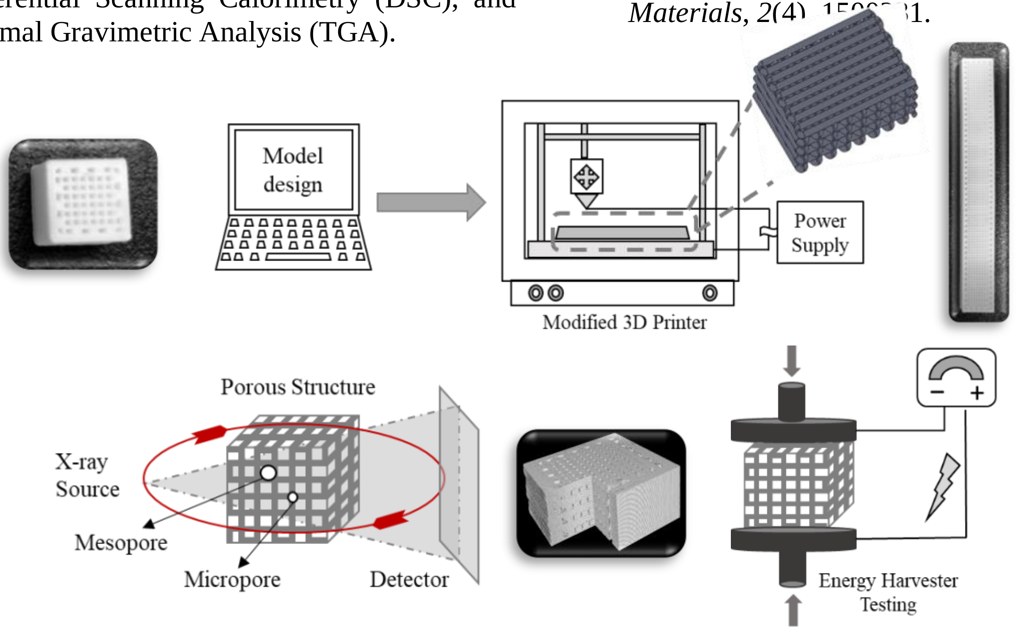


Figure 1: Graphical Abstract

Electrochemical detection of cymoxanil fungicide with new graphene modified glassy carbon electrode

C. Varodi [1*], A. Ciorita[1], A. Turza[1], F. Pogacean[1], M. Coros [1*], S. Pruneanu[1]
[1] National Institute for Research and Development of Isotopic and Molecular Technologies,
C luj-Napoca, Romania
codruta.varodi@itim-cj.ro; maria.coros@itim-cj.ro

Abstract:

Cymoxanil (CYM) or 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea is a based fungicides in agricultural practice. It is used in mixtures with another pesticides primarily to control downy mildew diseases and is key in controlling the fungal pathogens from grapes, tomatoes and potatoes. In the some time the pesticides have nocive effect on the environment and human health.

A lot of pesticides are identified and quantified with chromatographic methods, such as gas chromatography or high-performance liquid chromatography coupled with mass spectroscopy. In this work we propose a low cost and simple electrochemical detection of cymoxanil fungicide with a new graphene modified glassy carbon electrode.

We prepared graphene-based material doped with nitrogen and boron, denoted Gr-NB, by hydrothermal synthesis using graphene oxide, ureea and boric acid as precursors. The new material was morphologically and structurally characterized by SEM, FTIR, XRD and XPS and was used for the modification of glassy carbon electrode, denoted GC/Gr-NB. The pH influence (Figure 1) and the electrochemical performances for the Cymoxanil detection with the new graphene-modified electrode were compared with unmodified electrode and tested by cyclic voltammetry and linear sweep vol-tammetry in Britton Robinson buffer (BR). The electroanalytical parameters of GC/Gr-NB electrode (Figure 2) are very good and allow real sample analysis.

Ackowledgement: *This work was supported by grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number* PN-III-P4-ID-PCCF-2016-0006, *within PNCDI-III.*

Keywords: graphene, pesticide, electrochemical detection, cymoxanil

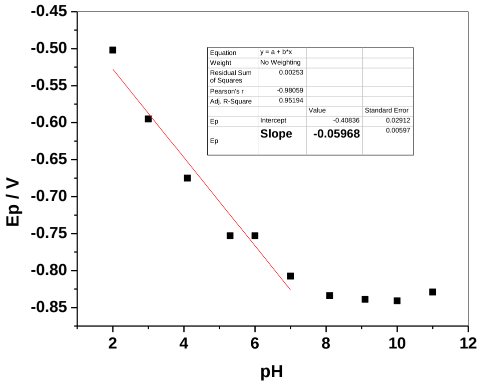


Figure 1: Figure illustrating the pH effect on the electrochemical reduction of CYM on the GC/Gr-NB electrode.

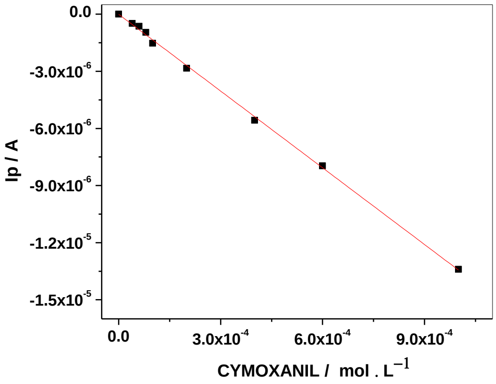


Figure 2: The resulting calibration curve for the electrochemical detection of CYM in pH6 BR with GC/Gr-NB electrode.

References:

1. Grimalt, S., Dehouck, P. (2016) Review of analytical methods for the determination of pesticide residues in grapes, *Journal of Chromatography A*, 1433, 1–23
2. Morrica, P., Fidente, P., Seccia, S. (2005), High-performance liquid chromatographic mass spectrometric identification of the photo-products of cymoxanil. *Biomed Chromatogr* 19:506–512.
3. Hengel, M.J., Shibamoto, T. (2001) Development of a gas chromatographic method for fungicide cymoxanil analysis in dried hops. *JAgric Food Chem*, 49, 570–573

Molecular Dynamics of Graphene-Electrolyte Interface: Effects of Charged Graphene on Interfacial Solution Structure and Molecular Diffusion

J. Dočkal [1,2,*], M. Lísal [1,2], F. Moučka [1,2]
[1] Department of Physics, Faculty of Science, J. E. Purkinje University , Czech Republic
[2] Department of Molecular and Mesoscopic Modelling, Institute of Chemical Process Fundamentals of the CAS , Prague, Czech Republic

Abstract:
Graphene-based applications often take place in aqueous environments, and they benefit from a molecular-level understanding of aqueous salt solutions in contact with graphene surfaces under different conditions. We study influence of positively and negatively charged graphene on the interfacial structure and adsorption of ions to the graphene sheet for aqueous electrolytes (LiCl, NaCl, KCl) using classical molecular simulations. In order to model the graphene–ion interactions accurately, we use the effective polarizable model of Williams *et al.* (*J. Phys. Chem. Lett.* 2017, 8, 703). We thoroughly characterize the solution structure at the graphene surface by standard structural properties and we also employ our novel intermolecular bond definition based on the spatial distribution functions, which provides numbers of water–water and water–ion intermolecular bonds per water molecule and number of water molecules per ion as functions of the distance from the graphene surface in a completely self-consistent manner. We explain the observed behavior by detailed analysis of particle distributions, rotations and structure of H-bonding network and other intermolecular bonds. Finally, we evaluate the lateral mobility of water and ions separately in the interfacial and bulk regions.

Keywords: graphene, molecular simulations, adsorption, diffusion, hydrogen bonding, aqueous eletrolytes, electrical double layer.

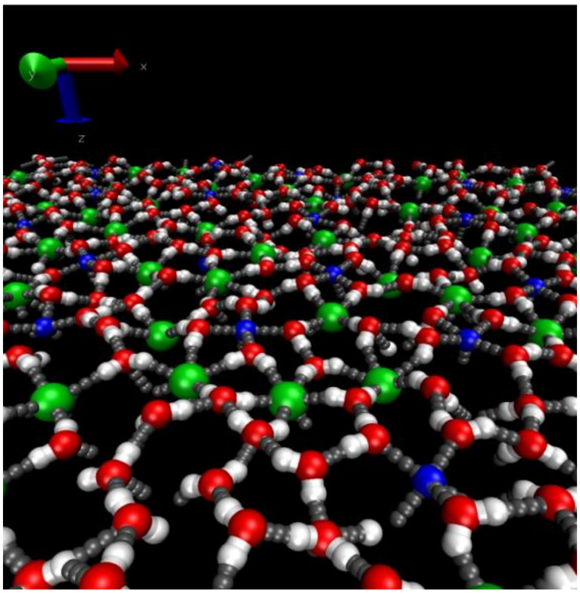


Figure 1: Figure illustrating structure of H-bonding network of NaCl aqueous solution near the interface with positively charged graphene sheet.

References:

1. Dočkal, J., Lísal, M., Moučka, F. (2019), Molecular Dynamics of Graphene-Electrolyte Interface: Interfacial Solution Structure and Molecular Diffusion, *J. Phys. Chem. C*, 123, 43, 26379-26396.
2. Dočkal, J., Svoboda, M., Lísal, M., Moučka, F. (2019), A general hydrogen bonding definition based on three-dimensional spatial distribution functions and its extension to quantitative structural analysis of solutions and general intermolecular bonds, *Journal of Molecular Liquids*, 281, 225-235.

Synthesis of Heteroatom co-doped Graphene Nanostructures and their Applications

M Coroş*, F Pogăcean, C Varodi, A Turza, T Radu A Cioriţa and S Pruneanu
National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat, 400293 Cluj-Napoca, Romania, email: maria.coros@itim-cj.ro

Abstract:

Graphene brought a major progress in modern science being one of the most auspicious materials for application in the next generation of sensor devices. Graphene consists of a monolayer of sp^2 hybridized carbon atoms arranged in a hexagonal lattice and posses zero band gap and fast electron transfer at the edges/defect sites of the sheet [1]. Doping graphene with heteroatoms leads to improved properties in the final nanomaterials. The doping approach demonstrates enhanced applications in electrochemical applications. By doping graphene with heteroatoms the band gap may be tailored in such a way as to provide electrochemically active/inactive sites.

Usually, the heteroatom-doped graphene can be prepared via two ways: (a) one step co-doping- direct synthesis such as chemical vapor deposition, arc discharge and electrochemical methods, and (b) two step doped synthesis methods, which involve post treatment, like thermal annealing, hydrothermal synthesis [2]. Their methods of preparation have a strong influence on their properties and on the way the heteroatom is implanted into the graphene lattice.

We present here the synthesis of heteroatom (nitrogen, sulfur, boron) co-doped graphene by hydrothermal synthesis and thermal treatment (Figure 1).

Keywords: graphene doping, synthesis of co-doped graphene, electrochemical applications.

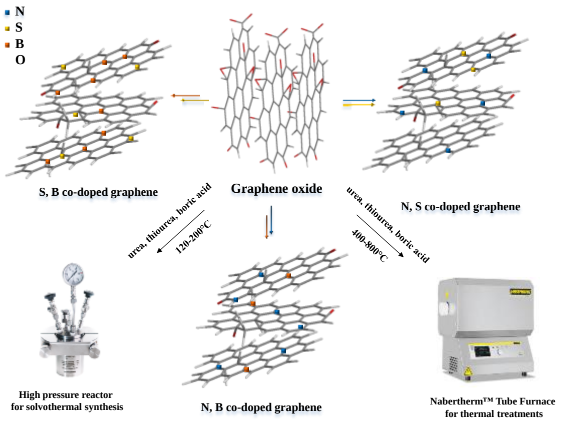


Figure 1: Illustration of different heteroatoms co-doped graphene materials obtained by solvothermal synthesis or thermal annealing.

Acknowledgements:

This work was supported by a grant of the Ministry of Research, Innovation and Digitization CNCS/CCCDI-UEFISCDI, project number PN-III-P4-ID-PCCF-2016-0006, within PNCDI III.

References:

1. Yang, G., Li, L., Lee, W.B., Ng, M.C. (2018) Structure of graphene and its disorders: a review. *Sci. Technol. Adv. Mater*. 19, 613–648.
2. Wang, X., Sun, G., Routh, P., Kim, D., Huang, W., Chen, P. (2014) Heteroatom-doped graphene materials: syntheses, properties and applications. *Chem. Soc. Rev*. 43, 7067–7098.

Electrocatalytic properties of NGr-ZnO hybrid materials

F. Pogacean*, M. Stefan, C. Varodi, M. Coros, L. Magerusan, V. Mirel, S. Pruneanu

National Institute for Research and Development of Isotopic and Molecular Technologies, Donat Street, no. 67-103, 400293, Cluj-Napoca, Romania; email: florina.pogacean@itim-cj.ro

Abstract:

N-doped graphene-ZnO hybrid materials with diferent N-doped graphene:ZnO wt% ratios (1:10; 1:20; 1:30) were prepared by a simple and inexpensive sol-gel method. The materials denoted NGr-ZnO-1 (1:10), NGr-ZnO-2 (1:20), and NGr-ZnO-3 (1:30) were investigated with advanced techniques and their morpho-structural, and electrocatalytic properties were reported. The X-ray powder difraction (XRD) investigation of N-doped graphene sample revealed that it was formed by a mixture of graphene oxide, few-and multi-layer graphene. After the ZnO nanoparticles were attached to graphene, major difraction peaks corresponding to crystalline planes of ZnO were seen. The qualitative and quantitative compositions of the samples were further evidenced by X-ray photoelectron spectroscopy (XPS). In addition, the electrocatalytic performances of glassy-carbon electrodes modified with the hybrid materials were investigated for the first time and compared with those of pure ZnO and N-doped graphene. The best CV parameters are those of the electrode modified with N doped graphene (GC/NGr) which reflects the characteristics of a reversible redox process: Ipa/Ipc ~ 1 and DEp ~ 60mV/n. In contrast, for all GC/NGr-ZnO modified electrodes, the parameters are considerably altered: Ipa/Ipc > 1 with larger peak potential separation, from 83 to 115 mV. This can be related to the gradual increase of ZnO concentration within the composite materials. For bare GC electrode, the peak potential separation exceeds 200 mV and the anodic/cathodic waves are very broad, indicating a quasi-reversible redox process.

Keywords: N-doped graphene-ZnO; hybrid materials; N-doped graphene-modified electrodes, electrocatalytic performances.

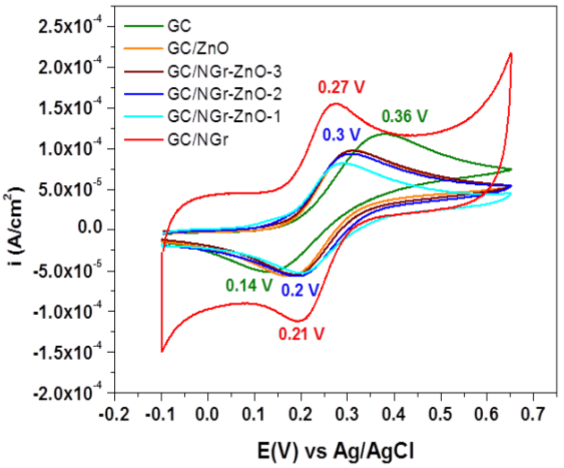


Figure 1: Cyclic voltammograms (current densities) recorded with bare glassy-carbon (GC) and GC-modified electrodes in 10^{-3} M $K_4[Fe(CN)_6]$ (0.2 M KCl supporting electrolyte); scanning rate 10 mV/s.

References:

1. Pogacean, F., Stefan, M., Toloman, D., Popa, A., Leostean, C., Turza, A., Coros, M., Pana, O., Pruneanu, S., (2020), Photocatalytic and Electrocatalytic Properties of NGr-ZnO Hybrid Materials, *Nanomaterials, 10, 8, 1473.*

Acknowledgement: This work was supported by grants of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCCF-2016-0006, and project number 500PED/2021, within PNCDI III.

Trifluoromethylphenyl-disubstituted derivatives of dimethylacridan and phenothiazine for multifunctional sensing and lighting applications

R. Keruckiene[1], Bo-Yen Lin[2], C.-H. Chen[3,4], C.-C. Chu[3], C.-F. Lin[5],
T.-L.Chiu[2], J.-H. Lee[3], J. V. Grazulevicius[1]

[1]Department of Polymer Chemistry and Technology, Faculty of Chemical Technology, Kaunas University of Technology, K. Barsausko st. 59-500, Kaunas, Lithuania
[2] Department of Electrical Engineering, Yuan Ze University, 135 Yuan-Tung Road, Chung-Li, Taoyuan, 32003, Taiwan
[3]Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University, 1, Sec.4, Roosevelt Road, Taipei 10617, Taiwan
[4]Department of Chemistry, National Taiwan University, 1, Sec.4, Roosevelt Road, Taipei 10617, Taiwan
[5]Department of Electro-Optical Engineering, National United University, 1, Lienda Road, Miaoli 36003, Taiwan

Abstract:

Development of efficient electroactive organic compounds is prerequisite for the fabrication of highly efficient OLEDs and other optoelectronic devices. A combination of donor and acceptor moieties in a single molecule enables to obtain efficient light-emitting materials exhibiting useful phenomena which allow to harvest triplet excitons formed under electrical excitation and convert them into light such as intramolecular and intermolecular (exciplex-based) thermally activated delayed fluorescence, room temperature phosphorescence (RTP), triplet-triplet annihilation etc. Owning to ultralong phosphorescence and dual emission (fluorescence+RTP) of some organic luminophores, these luminophores can be utilized for information identification in darkness (simply printing a barcode) or for lighting due to their white emission. The sensitivity of phosphorescence to oxygen can be utilized for oxygen sensing applications due to triplet states of oxygen lying in its electronic ground state (Figure 1). Strongly medium dependent capability to exhibit not only prompt/delayed thermally-activated fluorescence but also room temperature phosphorescence (RTP) or exciplex emission will be demonstrated either for solutions or for solid samples of acridan- and phenothiazine-based luminophores. Furthermore, green exciplex-based devices with EQE values reaching 7.6% will be presented.

Keywords: dimethylacridan; phenothiazine; exciplex; RTP; OLED.

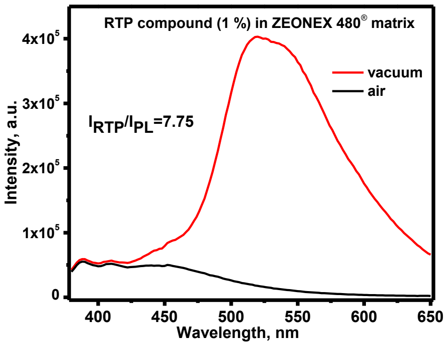


Figure 1: PL and RTP spectra of air-equilibrated and evacuated molecular dispersion of RTP compound in ZEONEX 480® matrix.

Acknowledgment: This research has received funding from European Social Fund (project No 09.3.3-LMT-K-712-19-0033) under grant agreement with the Research Council of Lithuania (LMTLT).

References:

1. Wang W., Liu Q., Zhan C., Barhoumi A., Yang T., Wylie R.G., Armstrong P.A., Kohane D.S. (2015), Efficient Triplet–Triplet Annihilation-Based Upconversion for Nanoparticle Phototargeting, *Nano Letters.* 15, 6332–6338.
2. Mei J., Leung N.L.C., Kwok R.T.K., Lam J.W.Y., Tang B.Z. (2015) Aggregation-Induced Emission: Together We Shine, United We Soar!, *Chem. Rev.* 115, 11718–11940.
3. Kabe R., Notsuka N., Yoshida K., Adachi C. (2016) Afterglow Organic Light-Emitting Diode, Adv. Mater. 28, 655–660.

Multifunctional silica-based sensors for real-time viral screening

P. Robin [1*], C.M.A. Journot [1], L. Mayoraz [1], D. Nicolis [2], L. Barnebei [3], C. Tiarantelli [3], L. Cascione [3], F. Lucarini [4], D. Staedler [4], F. Bertoni [3], I. Stefanini [2], S. Gerber-Lemaire [1]

[1]Institute of Chemical Sciences and Engineering, Group for Functionalized Biomaterials, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC SCI-SB-SG, Station 6, CH-1015 Lausanne, Switzerland;
[2]Department of Innovative Technologies, Institute of Systems and Applied Electronics, Scuola universitaria professionale della Svizzera, Via Mirasole 22A, CH-6500 Bellinzona, Switzerland;
[3]Institute of Oncology Research, Faculty of Biomedical Sciences, Scuola universitaria professionale della Svizzera, Via Vela 6, 6500 Bellinzona, Switzerland;
[4]TIBIO Services, Scitec Research SA, Avenue de Provence 18, CH-1007 Lausanne, Switzerland.

Abstract:

The emergence of the coronavirus disease in 2019 (COVID-19) highlighted the need for rapid, accurate and massive virus detection techniques to control the widespread of infectious diseases. Epidemic-causing mosquito-borne viruses such as Dengue, Zika or Chinkungunya, are under tight surveillance by sanitary organizations, as may be next to emerge on the global stage[1]. In Europe, although those viruses circulation is up to now limited, concerns have been raised about the recent emergence of Tiger mosquitos[2]. Monitoring potential arboviruses in the mosquitoes' established populations is of great interest for European health organizations to stay one step ahead.

We suggest an approach to address the limitations of current detection procedures using a low-cost and highly responsive biosensor, which would remove the need for biomedical personnel and advanced laboratory infrastructures. The biological samples could be taken from humans or any viral hosts and be processed to detect a variety of viruses.

Most viral detection techniques require the immobilization of biomolecules on a sensor surface. Silica-based materials are ideal sensor plateform for viruses due to their inexpensiveness, ease of functionalization and good temperature and mechanical stability[3].

We herein disclose a panel of surface conjugation strategies for the immobilization of single-strand DNA (ssDNA) probes on silica-based slides. Depending on the surface coating, both covalent immobilition or adsorption through electrostatic interactions will be studied. The resulting sensing platforms will be assessed for SARS-COV-2 and Zika detection. Fluorescence and bioimpedance measurements were chosen for the detection of the hybrization events between the viral RNA strands from the biological samples and the immobilized ssDNA strands (Figure 1). The orientation and density of the ssDNA probes at the surface of the sensor are known to play a major role on the efficacy of hybridization events[4]. Therefore, variation of size, branching degree, density and functionality of the polymers as well as adjuvants will be investigated for optimal sensor sensitivity.

Keywords: Viral sensor, SARS-COV-2, arboviruses, silica-based biomaterials, surface functionalisation, microfluidics, fluorescence, bioimpedance, RNA hybridization detection.

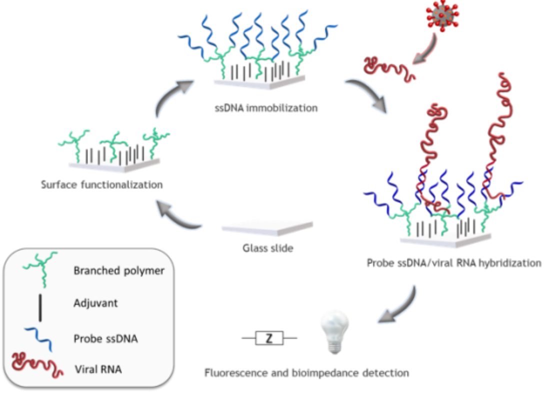


Figure 1: Preparation of ssDNA functionalized glass slides and their application for impedimetric or fluorescence detection of viruses.

References:

1. Kading, Rebekah C., Brault, Aaron C., Beckham, J. David. (2020), Global Perspectives on Arbovirus Outbreaks: A 2020 Snapshot, *Trop. Med. Infect. Dis.* 5(3), 142.
2. Ryan, Sadie J. (2019), Global expansion and redistribution of Aedes-borne virus transmission risk with climate change, *PLoS Negl Trop Dis*. 13(3), e0007213.
3. Wittmann, C., Bier, F. F. (2005). Immobilisation of DNA on chips II. *Springer*.
4. Campàs, M., Katakis, I.. (2004), DNA biochip arraying, detection and amplification strategies, *Trends Anal. Chem.*, 23(1), 49-62.

Two-dimensional Pnictogens (Monoelemental Nanosheets of Bi or Sb) as Transducing Materials in Electrochemical Sensing

A. Lazanas, M. Prodromidis*

Laboratory of Analytical Chemistry, University of Ioannina, 45 110 Ioannina, Greece

Abstract: The successful utilization of two-dimensional materials on modern day electroanalysis has been a desideratum ever since the emergence of graphene in 2004. To this day many other 2D materials such as transition metal dichalcogenides (TMDs), transition metal oxides (TMOs), MXenes etc. have gained significant attention due to their exotic properties, which have in many occasions ameliorated the performance of diverse electrochemical sensing devices [1]. Another important family of 2D materials derived from the elements belonging to the Group 15 of the periodic table (also known as ‘pnictogens’), with the most prominent member of this family, phosphorene (the 2D analog of black phosphorus), having been extensively studied in the past decade. Bismuthene and antimonene are also two promising 2D materials belonging in this group, which have already been utilized in many energy related applications such as OLED devices, lithium storage, supercapacitors etc. but have scarcely been reported in the field of electroanalysis.

Our work focuses on the liquid-phase exfoliation and implementation of these materials in anodic stripping voltammetry of heavy metal ions, as well as the cathodic voltametric determination of nitroaromatic copounds. Excessive characterization of the materials produced during this study includes morphological characterization with scanning electron spectroscopy and dynamic light scattering, Raman and FT-IR spectroscopy, crystallographical studies, as well as electrochemical characterization pertaining electrochemical impedance spectroscopy and cyclic voltammetry.

Bulk bismuth was exfoliated by a facile and fast shear-force liquid phase exfoliation method, while bismuthene colloids were mixed with dispersions of few-layer graphene, which was used as supporting material in order to achieve the desired adherence of bismuthene films onto the surface of glassy carbon electrode (GCE) as well as to achieve an effective electrical communication between them and with the electrode surface. Bismuthene/graphene/GCEs showed an excellent analytical performance on the simultaneous determination of Cd(II) and Pb(II) over the concentration range 1– 30 ppb as well as for the fast and accurate screening of tap water samples.

Data also demonstrated superior electrocatalytic performance for an antimonene oxide /PEDOT:PSS composite, which was produced in-situ by probe sonication of bulk Sb and PEDOT:PSS in water, towards the electro reduction of 4-nitrotoluene and 2,4-dinitrotoluene. The antimonene oxide /PEDOT:PSS composite-modified SPEs showed a linear response over the concentration range 50 – 1000 nM and 100 – 4000 nM, respectively. The method was also applied to the determination of the targets in spiked tap water samples. Recoveries were 102 and 103%, respectively.

Keywords: Pnictogens, liquid exfoliation, nanosheets, bismuthene, antimonene, electroanalysis, screen-printed electrodes

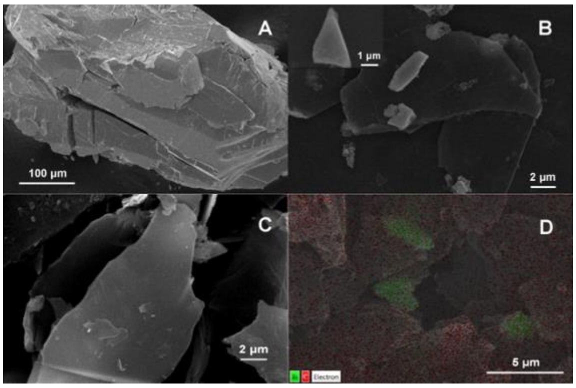


Figure 1: SEM images of (A) bulk bismuth, (B) few-layer bismuthene, (C) few-layer graphene, and (D) EDX mapping analysis of the bismuthene/graphene nanocomposite.

Reference:

[1] Lazanas, A., Prodromidis, M., (2021) Two-dimensional inorganic nanosheets: production and utility in the development of novel electrochemical (bio)sensors and gas-sensing applications, *Microchim. Acta,* 188, 6.

3D-Sparking Head Aided Screen-Printed Electrode-to-Graphite Pencil In-situ Tailoring of Sensing Surface with Graphitic Nanomaterials: Application to the Determination of Guanine and Adenine in Saliva and of 8-hydroxy-2´-deoxyguanosine in Urine

M. Trachioti[1], A. Papavasileiou[1], J. Hrbac[2], M. Prodromidis[1,*]
[1] Laboratory of Analytical Chemistry, University of Ioannina (UoI), 45 110 Ioannina, Greece
[2] Department of Chemistry, Masaryk University, 625 00 Brno, Czech Republic

Abstract:

Herein, we report on the fast (ca. 14-16 s), green (in the absence of any liquids), and direct generation of graphite nanomaterials (GNMs) through an electric discharge (sparking) process between pencil leads and graphite screen-printed electrodes (SPEs), at ambient conditions, by using a 3D-positioning sparking setup. Sparked GNM−SPEs were characterized by Raman spectroscopy, SEM, CV, and EIS. Data demonstrated the generation of sponge−like graphite nanostructures and low dimensional few−layer graphite flakes that endow SPE with outstanding electrocatalytic properties towards the electro-oxidation of guanine and adenine in saliva, and 8-hydroxy-2´-deoxyguanosine (8−OHdG) in urine.

Guanine and Adenine in Saliva: Guanine and adenine are two of the most important components of DNA and RNA molecules and abnormal changes on their levels in biological fluids indicate deficiency in the immunity system and metabolic human disorders. Elevated levels of guanine and adenine in biological fluids is indicative for mutations and oxidative stress associated with various diseases. Sparked GNM−SPEs enabled the simultaneous determination of guanine and adenine over the concentration range 5-1000 and 25-1000 nM, while LODs (S/N 3) were 2 and 8 nM, respectively. The sensor was successfully applied to saliva samples, after their filtration through 3 kDa MWCO centrifugal tubes to alleviate fouling phenomena of the sensing surface. The method was able to determine the targets at concentrations as low as 250 nM guanine and 500 nM adenine, while the accuracy of the method was examined by recovery studies in spiked saliva samples. Recovery was 96 – 108%.

8-hydroxy-2´-deoxyguanosine in urine: Oxidative DNA damage caused by the attack of reactive oxygen species could bring about several of diseases such as carcinogenesis, aging, diabetes, neurological disorders. Among various oxidative product of DNA damage, 8−OHdG is considered as one of the most important biomarkers. Sparked GNM−SPEs showed a linear response over the concentration 2-50 nM 8−OHdG, while the LOD (S/N 3) was 0.35 nM. The sensors were successfully applied to the determination of 8-OHdG in synthetic 10-fold diluted urine samples. The recovery of the method was evaluated at samples fortified with 300 and 400 nM 8−OHdG by using the standard addition method. Recovery values were 95.3 and 90.0%, respectively.

Keywords: Fast and green generation of carbon nanomaterials; Sparking; Biomarkers; Saliva and Urine analysis; Guanine and Adenine; 8-hydroxy-2´-deoxyguanosine;

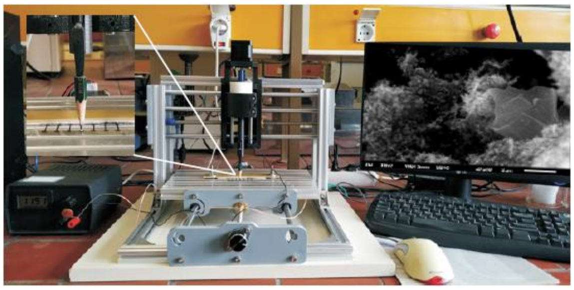


Figure 1: In situ modification of the graphite SPEs with the 3D-head spaking device.

References:

Trachioti, M., Hemzal, D., Hrbac, J., Prodromidis, M. (2020), Generation of graphite nanomaterials from pencil leads with the aid of a 3D positioning sparking device: Application to the voltammetric determination of nitroaromatic explosives, *Sens. Actuators B*, 310, 127871

Combining Health Coaching with Remote Monitoring: A Study of the Effectiveness for Hypertension Patients

Carl Markert[1], Karim Zahed[1], Farzan Sasangohar[1*]
[1]Department of Industrial and Systems Engineering, Texas A&M University, College Station, TX, USA

Abstract:
Hypertension is a chronic disease that affects people of all ages and is defined as a systolic blood pressure ≥ 130 mm Hg or a diastolic blood pressure ≥ 80 mm Hg (Centers for Disease Control and Prevention, 2020). Uncontrolled hypertension can lead to the development of other chronic health conditions including heart disease, stroke, kidney disease, pregnancy complications, and cognitive decline in later life (U.S. Department of Health and Human Services, 2020). Total annual medical costs in the U.S. associated with hypertension are currently estimated at $131 to $198 billion annually and projected to exceed $220 billion annually by 2035 (U.S. Department of Health and Human Services, 2020). In addition, this same report states that health care services are estimated to be approximately $2,500 more per year for people with hypertension compared to those without hypertension. Some additional facts about hypertension provided on the CDC website (Centers for Disease Control and Prevention, 2020) include:

- Hypertension was a primary or contributing cause of nearly 500,000 deaths in the U.S. in 2018.
- Approximately half of adults in the U.S. suffer from hypertension.
- Approximately 37 million adults in the U.S. have a blood pressure of 140/90 mm Hg or higher.
- Only about 1 in 4 adults suffering from hypertension have their condition under control.

Hypertension can be attributed to unhealthy lifestyle choices, such as a poor diet and sedentary lifestyle and certain health conditions, such as diabetes and obesity (Centers for Disease Control and Prevention, 2020). Adoption of healthy behaviors can engage patients in their treatment and promote self-management of hypertension. Mobile Health (mHealth) is the use of mobile computing and communication technologies in healthcare and can facilitate data collection and enable self-management of chronic conditions such as hypertension (Owen et al., 2015). mHealth shows promise in supporting health coaching, a patient-centered process based upon behavior change theory which includes goal-setting, education, encouragement, and feedback on health-related behaviors (Oliveira et al., 2017). However, the impact of mHealth coaching on self-management outcomes including changes in beliefs about intervention, quality of life, clinical outcomes, and actual engagement with an intervention is not well understood.

The HyperCoach app was developed by researchers at Texas A&M University as a mHealth coaching app to assist hypertension patients with the self-management of their disease. We partnered with the American Heart Association (AHA) to design a 30-day hypertension plan. The plan pushes coaching (feedback, education, and assessment) content via a mobile app over 30 days. An at-home pilot study was designed to assess the effects of health coaching enabled by a mobile platform and the 30-day AHA plan on health outcomes, compliance rates, and quality of life.

This study recruited 36 hypertension patients who were provided with Bluetooth enabled blood pressure (BP) and body weight scales that communicated via Bluetooth with a custom-designed Hypertension monitoring app (HyperCoach). The HyperCoach app enables automatic collection of BP and weight readings and transmission of the data to a cloud-based server. It provides coaching information in the form of data visualization of these measurements in daily and trend chart form. During the first 30 days of the study, the participants were provided with a limited version of the app that only reminds them to take BP and weight measurements and shows them their daily values and trends. During the second 30 days of the study, participants were provided with the full coaching version of the app. In addition to daily reminders to record BP and body weight measurements, participants were provided with a daily task to either watch an educational video, read an educational pamphlet, or to take a quiz/assessment from the AHA 30-day hypertension plan.

Keywords: hypertension, remote monitoring, digital coaching, human-computer interaction

References:

1. Centers for Disease Control and Prevention. (2020, May 19). High Blood Pressure Symptoms, Causes, and Problems. Centers for Disease Control and Prevention. https://www.cdc.gov/bloodpressure/about.htm
2. Centers for Disease Control and Prevention. (2020, September 8). Facts About Hypertension. Centers for Disease Control and Prevention. https://www.cdc.gov/bloodpressure/facts.htm
3. Oliveira, J. S., Sherrington, C., Amorim, A. B., Dario, A. B., & Tiedemann, A. (2017). What is the effect of health coaching on physical activity participation in people aged 60 years and over? A systematic review of randomised controlled trials. British Journal of Sports Medicine, 51(19), 1425–1432. https://doi.org/10.1136/bjsports-2016-096943
4. Owen, J. E., Jaworski, B. K., Kuhn, E., Makin-Byrd, K. N., Ramsey, K. M., & Hoffman, J. E. (2015). mHealth in the wild: Using novel data to examine the reach, use, and impact of PTSD Coach. JMIR Mental Health, 2(1), e7. https://doi.org/10.2196/mental.3935
5. U.S. Department of Health and Human Services, S. (2020). The Surgeon General’s Call to Action to Control Hypertension. Washington, DC: U.S. Department of Health and Human Services, Office of the Surgeon General.

Molecular layering method as base for producing of smart materials

N.V. Zakharova, A.A. Malygin
Department of chemical nanotechnology and of materials for electronic equipment products, St. Petersburg State Technological Institute (Technical University), SPbGTI(TU), Saint-Petersburg, Russia

Abstract:
The report discusses the results on the application of the Molecular Layering (ML) method in the creation of "smart" materials for various types of sensors.

The ML method is based on the chemisorptions of reagents on a solid substrate surface. The main idea of realization of the ML method is consists in consecutive escalating of monolayers of structural units of the set chemical composition on a surface of solid matrix (Figure. 1). The ML technique gives the possibility to form a wide variety of nanolayers (mono- and multilayer, multicomponent layers) on the surface of different solids (organic and inorganic powders, fibres, films etc.) with any geometrical form.

Main advantages of the developed technology over traditional surface processing methods are as follows:

- strong (chemical) binding of sorbates with the substrate surface;
- homogenous distribution of heterocomponents over the surface, i.e., high conformity of covering;
- a possibility to control the surface layer composition down to one monomolecular layer and to put different atomic layers one-by-one and to form multicomponent regular structures;
- low power consumption due to the use of chemical reaction heat for the synthesis;
- simplicity and flexibility of design that allows synthesizing materials for different purposes without additional investments.

Sorption and indicator properties of the granulated silica gels modified by matrix treatment by vanadium oxochloride vapors was investigated. These samples were highly sensitive coloured indicators of H_20, H_2S and NH_3.

Using the ML method, nanostructured mixed TiO_x – VO_x films have been synthesized that are promising for detecting oxygen over a wide range of concentrations at low operating temperatures of 150–300 °C. A sufficiently high degree of selectivity has been found when detecting oxygen, in comparison with other analyte gases (NH_3, H_2, CH_4 and CO_2).

Results obtained in a study of the properties of titanium- and aluminum-oxide nanocoatings synthesized by the ML method on the surface of quartz optical fibers also are presented. It is shown that, as the thickness of a titanium-oxide layer on the edge surface of a light guide increases, a cyclic change is observed in the power reflected from the fiber edge under the action of laser light. Aluminum-oxide nanocoatings on the extended side surface of the sheath of quartz fiber improve its heat resistance and mechanical bending strength. The results made it possible to significantly raise the reliability and extend the functional characteristics of fiber-optic pressure, temperature, and vibration sensors based on modified fibers in their service under extreme conditions.

Keywords: Molecular layering method, surface, gas sensor, nano-coating

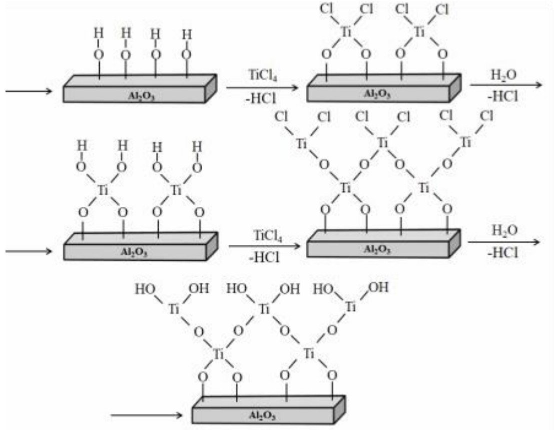


Figure 1: Scheme of obtaining oxide coatings on an Al_2O_3 plate by ML method.

This research is carried out in the 1st All-Russian Engineering Centreof the Molecular Layering Technology, Saint-Petersburg State Institute of Technology, with the financial support of the Ministry of Science and Higher Education of the Russian Federation (agreement № 075-15-2021-028).

References:

1. Malygin, A. (1996) Molecular Layering Technology and some of its applications, *Russian Journal of Applied Chemistry*, v. 69, 1419 – 1426.
2. Mokrushin A., Simonenko E, Simonenko N,

Zaharova N. (2019) Oxygen detection using nanostructured TiO_2 thin films obtained by the molecular layering method, *Appl. Surface Sci.*, v. 463, 197-202.

Iterative non-negative constrained deconvolution for waveguide enhanced Raman spectroscopy signal recovery

Zhen Liu[1], Mohamed A. Ettabib[1], Bethany M. Bowden[2], Almudena Marti[2], Philip N. Bartlett[2], James S. Wilkinson[1], and Michalis N. Zervas[1,*]
[1] Zepler Institute for Photonics and Nanoelectronics, University of Southampton, Southampton SO17 1BJ, UK
[2]School of Chemistry, University of Southampton, SO17 1BJ, UK

Abstract:

Waveguide enhanced Raman spectroscopy (WERS) provides a promising optical sensing method but suffers from inevitable noise and Raman signal peak broadening. Post-processing is valuable to recover the useful information, but conventional denoising algorithms suffer from the contradicting requirements of preserving subtle signal features and eliminating the noise. In addition, ringing artifacts are unavoidably introduced when deconvolution is applied, which can generate false peaks in the spectrum.

Here we report a group of accumulative and interdependent algorithms to recover the Raman spectrum. As a pre-deconvoluting step for increasing the signal-to-noise ratio and avoiding the amplification of noise peaks, the non-local means (NLM) [1] algorithm, used extensively in 2D image denoising, has been utilized. It has been developed to a multi-frame base NLM algorithm to denoise the 1D Raman signal and shows an improved capability of preserving subtle signal peaks while eliminating the noise when compared with standard wavelet denoising (see Figure 1). Conventionally, the deconvolution and baseline subtraction of the Raman signal are two independent processing steps. However, requiring that the deconvolved spectrum should be always above the baseline, sets up a non-negative constraint for the deconvolution and makes the two steps interdependent. In our algorithm, the baseline subtraction and spectrum deconvolution are obtained through successive iterations. The baseline subtraction is realized by the asymmetric least square method [2] with the improvement of applying the kernel method (radial basis function is used here), which enables the algorithm to find the baseline more accurately and swiftly. As shown in Figure 2, the deconvoluted spectrum, compared to the simulation by Gaussian^{TM}, shows successful recovery of the degraded multi-peaks with suppressed ringing artifacts and simultaneous baseline removal. More processed data with quantified evaluation will be presented.

Keywords: waveguide enhanced Raman spectroscopy, Raman spectrum, non-local means, non-negative constrained deconvolution, asymmetric least square, radial basis function

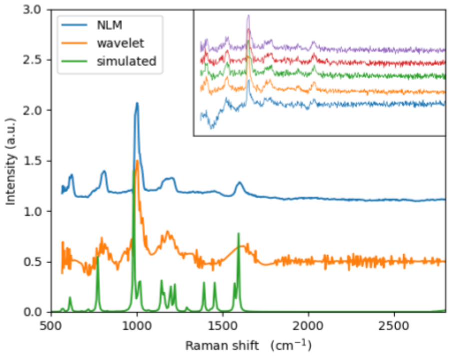


Figure 1. Multi-frame based NLM denoising for Raman spectrum of benzyl alcohol and comparison with results of wavelet decomposition based filtering and simulation by Gaussian^{TM}. The inset shows the raw 5 frames of the spectrum from WERS.

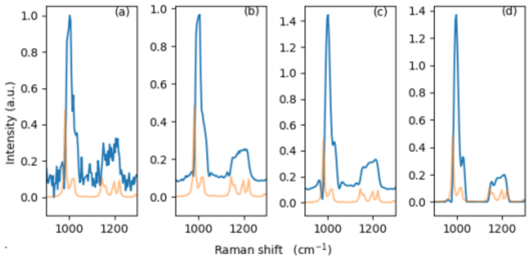


Figure 2. Illustration of the accumulative processing steps. (a) Raw spectrum of benzyl alcohol from WERS. (b) NLM denoised spectrum. (c) Blind deconvolution. (d) Baseline removal and non-negative deconvolution. The orange curve is the simulated spectrum by Gaussian^{TM}.

References:

1. A. Buades, B. Coll, and J.-M. Morel. (2011) *Image Processing On Line*, 1, 208–212, doi: 10.5201/ipol.2011.bcm_nlm.
2. J. Peng, S. et al. (2010) *Anal. Chim. Acta*, 683, 63–68, doi: 10.1016/j.aca.2010.08.033.

High Triplet Energy Aryl Sulfones for Exciplex-Based White Electroluminescent Devices

J. Keruckas[1], X. Tan[1], D. Volyniuk[1], J.V. Gražulevičius[1], R.S. Bernard[1], U. Tsiko[1],
K. Ivaniuk[2], I. Helzhynskyy[2], P. Stakhira[2]
[1] Department of Polymer Chemistry and Technology, Kaunas University of Technology,
Kaunas, Lithuania
[2] Department of Electronic Devices, Lviv Polytechnic National University, Lviv, Ukraine

Abstract:

Several organic compounds intended as light-emitting materials for optoelectronic applications were developed and investigated. These are comprised of diphenyl sulfone as electron acceptor with phenoxazine (**1**), phenoxathiine (**2**), and xanthene (**3**) as electron donor units (Figure 1).

Some important characteristics of these materials such as emission spectra, singlet (S) and triplet (T) energy levels as well as ionization potentials (I_p) and energy band-gaps (E_g) are determined by the donor moiety: S, T, and I_p increase with decreasing donor strength going from phenoxazine to xanthene while E_g tends to decrease.

The derivative of xanthene **3** showed the highest S and T levels of respectively 4.0 and 3.0 eV among the compounds investigated. Its fluorescence and phosphorescence spectra are situated in near UV and blue-green regions, respectively. Compound **3** has formed efficient blue and yellow light emitting complexes (exciplexes) with respective commercial electron donating carbazolyl- and diphenylamino-substituted triphenylamines. Both exciplexes were employed in organic light-emitting device (OLED) to produce white light. The OLED was fabricated using layer-by-layer vacuum deposition technique. The exciplex emission in the device was realized at the interface between the layers of compound **3** and the mentioned triphenylamines. The overall electroluminescence (EL) of the OLED resulted as superposition of EL of both exciplexes.

The emission of the fabricated OLED was characterized by CIE colour coordinates of (x = 0.29, y = 0.37) which are close to natural white light (x = 0.33, y = 0.33). The fabricated OLED exhibited turn-on voltage of 4.8 V, maximum luminescence of 18.5×10^3 cd/m^2, and maximum external quantum efficiency (EQE) of 10.6% which is close to the best all-exciplex-based white OLED the EQE of which has reached 11.6%.

Keywords: aryl sulfone, exciplex, electroluminescence, white organic light-emitting diode.

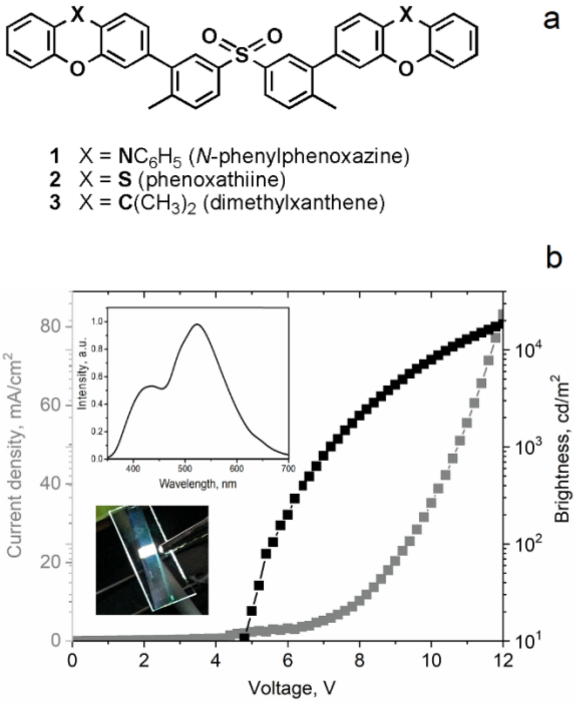


Figure 1: Chemical structure of the reported aryl sulfones (a); emission spectrum and performance characteristics of white OLED (b).

References:

1. Tan, X., Volyniuk, D., Matulaitis, T., Keruckas, J., Ivaniuk, K., Helzhynskyy, I., Stakhira, P., Gražulevičius, J.V. (2020), High triplet energy materials for efficient exciplex-based and full-TADF-based white OLEDs. *Dyes Pigments*, 177, 108259.
2. Hung, W.-Y., Fang, G.-C., Lin, S.-W., Cheng, S.-H., Wong, K.-T., Kuo, T.-Y., Chou, P.-T. (2015), The first tandem, all-exciplex-based WOLED. *Sci. Rep.*, 4, 5161.

Acknowledgement:

This research has received funding from European Regional Development Fund (project No. 01.2.2-LMT-K-718-01-0015) under grant agreement with the Research Council of Lithuania.

Disposable amperometric aptasensor for Troponin I based on carboxyethylsilanetriol-modified graphene oxide coated electrodes

A. Villalonga [1*], I. Estabiel [1], A. M. Pérez-Calabuig [1], B. Mayol [1], C. Parrado [1], R. Villalonga [1]
[1] Department of Analytical Chemistry, Faculty of Chemistry, Complutense University of Madrid, Madrid, Spain

Abstract:
Cardiovascular diseases constitute a major health problem with pandemic dimensions, being the first cause of mortality in the world. Among these diseases, myocardial infarction (MI) is the most common and deadliest form, representing over 15% of all global deaths.[1] Early diagnosis and systematic monitoring is the key to improve the survival rate for MI patients. That is why, the development of portable and sensitive analytical methods for the prognosis and monitoring of MI biomarkers is a priority in clinical medicine.

Cardiac troponin testing has been the standard of practice for the diagnosis of MI, early rule-out, risk stratification, and outcomes assessment in patients presenting with acute coronary syndrome and non-acute coronary syndrome of myocardial injury. In special, cardiac troponin I (cTnI) is considered the "gold standard" for MI diagnosis because this protein is quickly and specifically released to the blood circulation after a heart damage.[2]

This work describes the construction of a novel amperometric aptasensor for the specific detection of cTnI, by using screen-printed carbon electrodes coated with a carboxyethylsilanetriol-modified graphene oxide derivative as transduction element. This novel carboxylic acid-enriched nanomaterial allows easy and high load immobilization of the capture aptamer molecules on the electrode surface. The biosensing interface was assembled by covalent attachment of an amino-functionalized DNA aptamer on the carboxylic acid-enriched electrode surface. The sensing approach relies on the specific recognition of cTnI by the aptamer and further assembly of a sandwich-type architecture with a novel aptamer-peroxidase conjugate as signaling element. The aptasensor was employed to detect the cardiac biomarker in the broad range from 1.0 pg/mL to 1.0 µg/mL with a detection limit of 0.6 pg/mL. This electroanalytical device also showed high specificity, reproducibility and stability, and was useful to quantify cTnI in reconstituted human serum samples.[3]

Keywords: Cardiac troponin I, aptasensor, aptamer, graphene, screen-printed electrodes

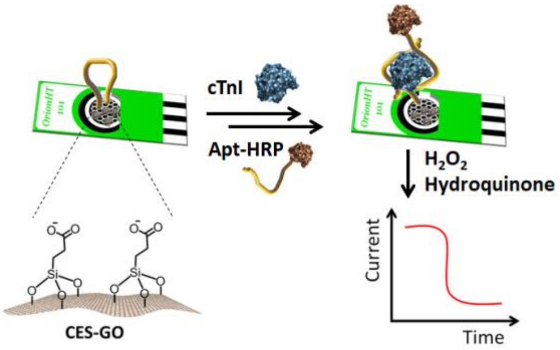


Figure 1: Schematic representation of the specific aptasensor for cTnI.

References:
1. Jayaraj, J. C., Davatyan, K., Subramanian, S. S., Priya, J. (2018). Epidemiology of myocardial infarction. In *Myocardial Infarction*, Ed. IntechOpen (pp. 9-19).
2. Park, K. C., Gaze, D. C., Collinson, P. O., Marbel, M. S. (2017) Cardiac troponins: from myocardial infarction to chronic disease. *Cardiovasc. Res.*, 113, 1708-1718.
3. Villalonga, A., Estabiel, I., Pérez-Calabuig, A. M., Mayol, B., Parrado, C., Villalonga, R. (2021), Amperometric aptasensor with sandwich-type architecture for troponin I based on carboxyethylsilanetriol-modified graphene oxide coated electrodes, *Biosens. Bioelectron.*, 183, 113203.

Monitoring of the evolution of human chronic wounds using a ninhydrin-based sensory polymer and a smartphone

S. Vallejos [1,*], M. Guembe-García [1], V. Santaolalla-García [2], N. Moradillo-Renuncio [2], S. Ibeas [1], J.A. Reglero [1], F.C. García [1], J. Pacheco [3], S. Casado [3], J.M. García [1]

[1] Departamento de Química, Universidad de Burgos, Burgos, Spain
[2] HUBU (Hospital Universitario de Burgos), Burgos, Spain
[3] Departamento de Economía Aplicada, Universidad de Burgos, Burgos, Spain

Abstract

The healing processes in cutaneous wounds, i.e., chronic wounds, represent a health problem affecting 1-2% of the population. The evaluation of these wounds is mainly based on subjective parameters, although there is a medical consensus on protease activity as the best marker for healing disorders. Here we show the correlation of the amino acid concentration on chronic wounds and with their evolution, and the development of a test kit to straightforward determining this evolution. Our test kit is a colorimetric sensory polymer film that change its colour upon contacting amino acids (based on ninhydrin receptor units). The kit allows for quantification of the overall amino acid concentration by simply analysing the colour definition parameters of the sensory film obtained from of a photograph taken with a smartphone. We analysed with the kit the amino acid concentration of human chronic wounds of 34 patients and we mathematically demonstrate that there is a correlation with the amino acid concentration, related with the protease activity, and the evolution of the wound's diagnoses. This kit can help diagnosis of human chronic wounds, usually evaluated and treated along time by different physicians, or even by different medical teams, providing an analytical tool not subjected to subjective evaluation.

Experimental

For the synthesis of a polymer with ninhydrin-based receptor units, the synthesis of a monomer with a reactive side moiety was performed following the same philosophy as in previous works.[1–3] Instead of carrying out the complete synthesis of the sensory monomer, we prepared a monomer which subsequent bulk radical initiated polymerization rendered a functional polymer film that was transformed into the sensory polymer containing ninhydrin-based receptors by straightforward solid phase synthesis. Compared to conventional monomer synthesis, this methodology is cost effective and greener, it reduces both the use of solvents and the time needed (see Scheme 1).

Results and Discussion

The state of the chronic wounds was determined by four parameters or pathologies: infectious appearance, bad evolution, necrosis and ischemia. Then, we compared these results with the amino acid concentration obtained by reference method and our proposed RGB_method. For this study, three linear classification methods were used: discriminant analysis (DA), logistic regression (LR) and support vector machine (SVM). With the observed data, a set of coefficients was determined (c_i) accompanying the explanatory variables, plus a free coefficient c_0. With these coefficients, the classification/diagnosis of a specific case was obtained by calculating the val parameter with an equation, where m is the number of explanatory variables and v_1,…, v_m are the values of these variables for this case. In this way, if val>0, the case is diagnosed positive (YES) and otherwise negative (NO).

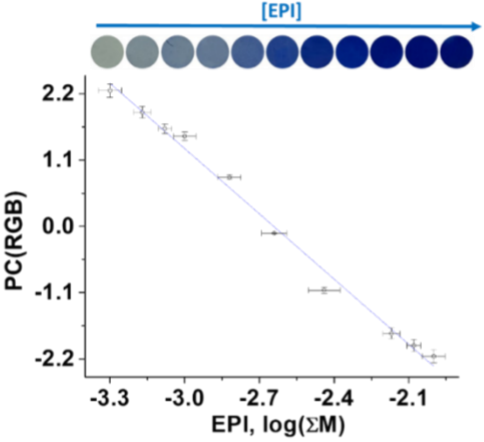


Figure 1. Titration of sensory polymer discs with solution mimicking epidermis (**EPI**) was performed with RGB_method. Discs of 8 mm diameter of **F_2** were dipped in pH 4.66 buffered solutions of **EPI**, with a sum of concentrations of all amino concentrations ranging from $5x10^{-4}$ to $1x10^{-2}$ M (ΣM). After reaction at 100°C for 60 min, the discs were washed several times with water, and photographed for the extraction of RGB data, which were simplified

to a single variable (principal component, **PC**) through a multivariate analysis.

Table 1 depicts the results obtained by the three methods considered, using the absorbance at 330 nm in the case of reference method ($m = 1$), and RGB parameters in the case of the RGB_method ($m = 3$) as explanatory variables for all analysed medical parameters. The results include the number of successes (Sc, i.e. number of correctly diagnosed cases), the ratio (rat, from 0 to 1), and the number of positive and negative cases for each parameter.

Table 1. Results obtained by the diagnostic methods using both reference method and RGB_method as explanatory variables

Experimental method	**Medical parameter**	**Cases**		**Analysis method**		
		No	**Yes**	**DA**	**LR**	**SVM**
Reference method	Infectious aspect	26	9	16 **(Sc)**	26	26
				0.4571 ***(rat)***	*0.7429*	*0.7429*
	Bad evolution	21	14	20	**24**	21
				0.5714	*0.6857*	*0.6*
	Necrosis	26	9	24	25	26
				0.6857	*0.7143*	*0.7429*
	Ischemia	28	7	24	27	28
				0.6857	*0.7714*	*0.8*
RGB_method	Infectious aspect	25	9	19	23	25
				0.5588	*0.6765*	*0.7353*
	Bad evolution	21	13	19	**22**	21
				0.5588	*0.6471*	*0.6176*
	Necrosis	25	9	21	**31**	25
				0.6176	*0.9118*	*0.7353*
	Ischemia	27	7	22	26	27
				0.6471	*0.7647*	*0.7941*

Concluding Remarks

We propose a new method and methodology for the control and diagnosis of chronic wounds based on pictures taken to discs cut from sensory films, which change their colour upon entering into contact with amino acids. The sensory polymeric material is inexpensively prepared by straightforward procedures from 99% of commercially available monomers. The experimental procedure is simple, neither reactants nor expensive equipment are needed, and can be straightforward carried out by untrained personnel by taking a photograph with a smartphone to the sensory material after immersing in the exudate. The sensor can be used in a broad pH range and has no interference with a vast number of anions and cations. Additionally, we have demonstrated that the state/evolution of the wound correlates with the concentration of amino acids. The chosen reference method for measuring amino acids (Nielsen method[4]) has shown to have good results in wound diagnosis. Mainly, in the case of bad evolution, the results are fascinating. In the other hand, it has been established that there is a functional relationship between the values of this reference method and the values of the digital colour of the photograph of the discs (R, G and B parameters). Even, the RGB values show to have a diagnostic capability of chronic wounds similar to the reference method, and better in the case of necrosis. We have used linear models, for data treatment and predictions, which are conceptually simple to understand and apply. However, more sophisticated models could significantly improve the quality of the results, and could be integrated into an easy to use software or smartphone app.

Acknowledgements

We gratefully acknowledged the financial support provided by Fondo Europeo de Desarrollo Regional and both the Spanish Ministerio de Economía, Industria y Competitividad (MAT2017-84501-R and ECO2016-76567-C4-2-R) and the Consejería de Educación, Junta de Castilla y León (BU306P18 and BU071G19).

Keywords: protein folding, nanoporous sol-gel glasses, silica-based biomaterials, circular dichroism spectroscopy, surface hydration, crowding effects, micropatterning, biomedical applications.

References:

1. Bustamante, S. E. et al. (2019) Polymer films containing chemically anchored diazonium salts with long-term stability as colorimetric sensors. *J. Hazard. Mater.*, 365, 725–732.
2. Vallejos, S. et al. (2018) Polymeric chemosensor for the detection and quantification of chloride in human sweat. Application to the diagnosis of cystic fibrosis. *J. Mater. Chem. B* 6, 3735–3741
3. Vallejos, S. et al. (2017) Direct visual detection and quantification of mercury in fresh fish meat using facilely prepared polymeric sensory labels. *J. Mater. Chem. A*, 5, 13710–13716.
4. Nielsen, P. M., et al. (2001) Improved Method for Determining Food Protein Degree of Hydrolysis. *J. Food Sci.*, 66, 642–646.

Impact of patch-potentials on capacitive displacement measurements

L. Daul [1*], I. Busch [1], T. Jin [2], L. Koenders [1], M. Weinert [1], H. Wolff [1]

[1] Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany
[2] School of Optical-Electrical and Computer Engineering, USST, Shanghai, 200093, China

Abstract:

Capacitive sensors used for dimensional measurements are an integral part of precision manufacturing. Among other things, they are characterized by their compactness and high measuring speed, however, they need to be calibrated [1]. Nevertheless, measurement deviations, like non-linearities, occur depending on the sensor geometry, the alignment, the quality of the electrodes surfaces and environmental conditions. Additionally, also local variations of work function of the electrode surface can have an impact on the measurement. These variations are due to local differences in chemical composition of metal alloys, grain boundaries in polycrystalline structures and surface adsorption. First, these so-called patch potentials cause a measurable attractive force between two plates [2]. Secondly, they have an impact on the propagation of electric field lines of capacitive displacement sensors. The influences of the different effects have been investigated in our study by Finite Element Method (FEM) simulation and experimental setup. For this purpose, a FEM model for capacitive sensors has been extended to invest the influence of changes in the lateral distribution of surface potentials as well as the magnitude of local changes on the distortion of the electric field, which is mainly responsible for non-linearities.

For experimental investigations, cylindrical electrodes are manufactured that correspond to commercially available sensors. The local change in surface Contact-Potential Differences (CPDs) is characterized using the Amplitude-Modulated Kelvin-Probe-Force-Microscopy (AM KPFM) mode of an AFM. Fig. 1 shows a KPFM measurement on a commercial capacitive sensor, where the CPD shows local variations of up to 255 mV. The variations of the local CPD on the special designed PTB sensors is up to 500 mV. However, repeated measurements indicate that the surface potentials are varying over time. In a second approach thin-film electrodes are manufactured by depositing and structuring aluminum on a silicon wafer. Using a lift-off process, rings of Au, Cr and Al with a thickness of 50 nm are applied to the aluminum surface. The geometry corresponds to the surfaces of the sensors in the FEM simulation. Due to the material contrast between the rings and the electrode surface, local, temporally stable differences of the surface potential are created. The local CPD amounts to 250 mV between the chromium rings and aluminum surface and 350 mV in the case of gold rings.

In the experimental setup, capacitive displacement measurements are performed with the thin film electrodes to investigate the influence of the number of rings on the slope error and nonlinearity.

Keywords: capacitive displacement sensors, patch potentials, nonlinearity, Kelvin-Probe Force Microscopy

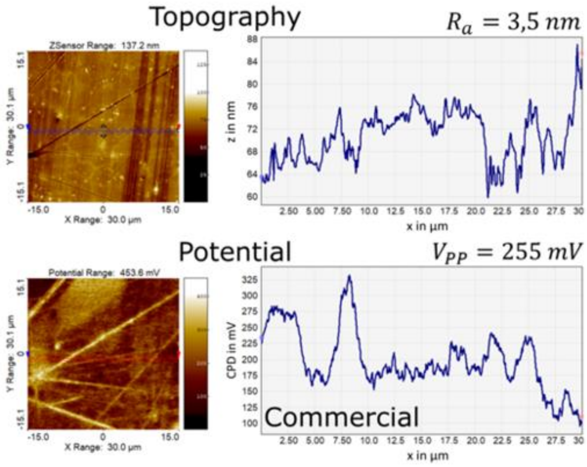


Figure 1: AFM measurement in KPFM mode on the surface of a commercial capacitive sensor. Local variation of the CPD amounts to 255 mV.

References

1. Haitjema, H. The Calibration of Displacement Sensors. *Sensors* 2020, *20*, 584.
2. Garrett, J.L.; Kim, J.; Munday, J.N. Measuring the effect of electrostatic patch potentials in Casimir force experiments. *Phys. Rev. Research* 2020, *2*, doi:10.1103/physrevresearch.2.023355.

Polymer-ceramic composites containing hydroxyapatite for supporting bone tissue regeneration

B. Tyliszczak [1*], M. Głąb [1], A. Drabczyk [1], S. Kudłacik-Kramarczyk [1], A. Sobczak-Kupiec [1]

[1] Department of Materials Science, Faculty of Materials Engineering and Physics, Cracow University of Technology, 37 Jana Pawła II Av., 31-864 Krakow, Poland, * bozena.tyliszczak@pk.edu.pl

Abstract:

Great attention is nowadays directed to the development of biomaterials for regenerative medicine which simultaneously deliver the active substance and provide appropriate conditions for osteointegration process. A promising material with a great potential for such an application is hydroxyapatite (HAp). This inorganic compound exhibits biocompatibility, non-immunogenicity and bioactivity. Furthermore, hydroxyapatite is characterized by an osteoinductivity, i.e. induces a process of osteogenesis. Next, hydroxyapatite shows also an osteoconductivity so forms an environment appropriate for cell growth and, importantly, enables to form a direct structural and functional connection between a composite containing HAp and a tissue. This is a reason why hydroxyapatite is widely applied for preparation of composites used in tissue engineering for filling bone defects.

Here, a synthesis and investigations on polymer-ceramic composites are discussed. Polyvinylpyrrolidone (PVP) and poly(vinyl alcohol) (PVA) were used for preparation of polymer matrix while hydroxyapatite powder was used as a ceramic phase. HAp was obtained via a wet precipitation method while polymer composites were prepared via a photopolymerization process using adequate crosslinking agent and photoinitiator. Performed studies allowed to characterize both a hydroxyapatite powder applied and polymer-ceramic composites obtained. Investigations aimed firstly at developing the synthesis methodology and compositions of composites and further evaluation of their swelling properties, surface morphology and chemical structure. Development of the synthesis methodology of composites as well as their physicochemical assessment is key to develop materials which may support bone repair and fill bone defects.

Keywords: polymer-ceramic composites, hydroxyapatite, osteointegration, bone repair, photopolymerization

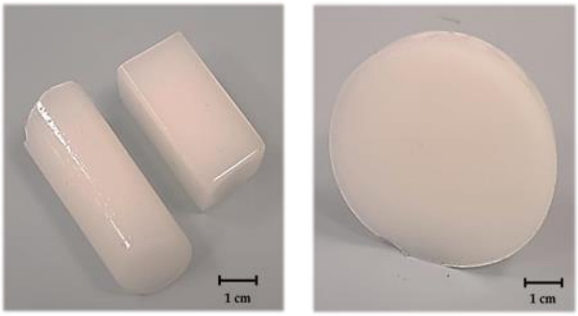


Figure 1: Figure illustrating obtained polymer-ceramic composites.

Acknowledgements: The “Multifunctional biologically active composites for applications in regenerative bone system medicine” project is carried out within the TEAM-NET program of the Foundation for Polish Science financed by the European Union under the European Regional Development Fund. POIR.04.04.00-00-16D7/18.

References:

1. Mondal, S., Pal, U. (2019) 3D hydroxyapatite scaffold for bone regeneration and local drug delivery applications. *J. Drug Deliv. Sci. Technol.* 53, 101131.
2. Alonzo, M., Primo, F.A., Kumar, S.A., Mudloff, J.A., Dominguez, E., Fregoso, G., Ortiz, N., Weiss, W.M., Joddar, B. (2021) Bone tissue engineering techniques, advances, and scaffolds for treatment of bone defects. *Curr. Opin. Biomed. Eng.* 17, 100248.

Smart composites as carriers of active substances

Agnieszka Sobczak-Kupiec[1], Dagmara Słota[1], Wioletta Florkiewicz[1], Karina Piętak[1], Mateusz Dyląg[1,2]
[1] Department of Materials Science, Faculty of Materials Engineering and Physics, Cracow University of Technology, Krakow, Poland
[2] ATMAT Company, Krakow, Poland

Abstract:

One of the biggest problems in contemporary medicine today is the lack of fully effective ways to cure cancer, which is currently the cause of death of more than 10% of the world's population. Present options to treat cancer are local approaches like radiation therapy or surgery and systemic ones such as hormone therapy or the most common, chemotherapy. However, chemotherapy involves many inconveniences, such as lack of specificity, side effects of the drugs taken, as well as multi-drug resistance, or distribution of the drug throughout the body. This reduces the chance of delivering the right dose to the affected area, ultimately forcing the dose to be increased.

The solution is to develop carrier-drug systems by incorporating selected pharmacologically important active substances and by controlled release of this substance at the affected site with the ability to monitor the location of the substance in the patient's body.

As a trasort carrier, liposomes, micelles, dendrimers, nanoshells, nanospheres or nanoparticles are used (Figre 1). Encapsulation of drugs in carriers, improves selectivity of their action in relation to disease-affected cells and tissues, minimizing unwanted systemic side effects and impact on healthy cells. Targeted therapy additionally allows for personalization of the administered drug dose based on individual patient needs.

Besides drugs, other active substances with high biological value can be encapsulated. The presented work focuses on the development of a ceramic-polymer composite carrier for active proteins, vascular endothelial growth factor or transforming growth factor.

The “Multifunctional biologically active composites for applications in regenerative bone system medicine” project is carried out within the TEAM-NET program of the Foundation for Polish Science financed by the European Union under the European Regional Development Fund. POIR.04.04.00-00-16D7/18.

Keywords: drug delivery system, hydrogels, composite, vegf, tgf.

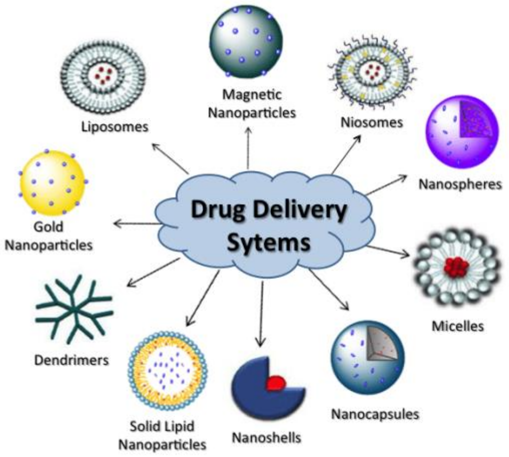


Figure 1: Drug delivery systems for the diagnosis and/or therapy of various diseases.

References:

1. Gunay, M.S., Ozer, A.Y., Chalon, S. (2016) Drug Delivery Systems for Imaging and Therapy of Parkinson’s Disease, *Current Neuropharmacology*. 14, 376-391.
2. Elsharkasay, O.M., Nordin, J.Z., Hagey, D.W., de Jong, O.G., Schiffelers, R.M., Andaloussi, S.E.L., Vader, P. (2020) Extracellular vesicles as drug delivery systems: Why and how?, *Advaced Drug Delivery Reviews*, 159, 332-343.

Polymer-ceramic composite coatings modified with active agents

Wioletta Florkiewicz[1], Dagmara Słota[1], Karina Piętak[1], Bożena Tyliszczak[1], Agnieszka Sobczak-Kupiec[1]

[1] Department of Materials Science, Faculty of Materials Engineering and Physics, Cracow University of Technology, 37 Jana Pawła II Av., 31-864 Krakow, Poland

Abstract:

Polymer-ceramic composite coatings show exceptional application potential in various biomedical applications due to the possibility of their modification in a wide range. Composite coatings are used to give the surface of the material additional functionality. The purpose of such modifications is primarily to meet specific requirements for materials, by adapting their operation to specific biomedical applications. Modifications of composite coatings allow to support cell proliferation, tissue growth, and also enable the delivery of various types of biomolecules such as growth factors, compounds with antimicrobial activity and drugs [1].

Due to such significant functionalisation possibilities of biocoatings, they can play a key role in the development of next-generation biomaterials. Polymer coatings can be produced using various methods, layer by layer (LBL) deposition, Langmuir-Blodgett method, plasma coating, as well as immersion and spin-coating, and by the production of polymer brushes or hydrogel coatings [2]. In addition to polymers such as polypropylene (PP), polydimethylsiloxane (PDMS) and polyvinylpyrrolidone (PVP), also other biopolymers such as polylactic acid (PLA), polyethylene (PE) and some naturally derived polymers, e.g. collagen and chitosan, are also used to produce coatings on implantable biomaterials [3].

The combination of the properties of polymers with bioactive ceramics and active substances, e.g. drugs, growth factors, or substances of natural origin such as flavonoids may result in the development of materials with antimicrobial activity and supporting tissue regeneration.

The “Multifunctional biologically active composites for applications in regenerative bone system medicine” project is carried out within the TEAM-NET program of the Foundation for Polish Science financed by the European Union under the European Regional Development Fund. POIR.04.04.00-00-16D7/18.

Keywords: composite coatings, hydrogels, antibacterial agents, bone regeneration .

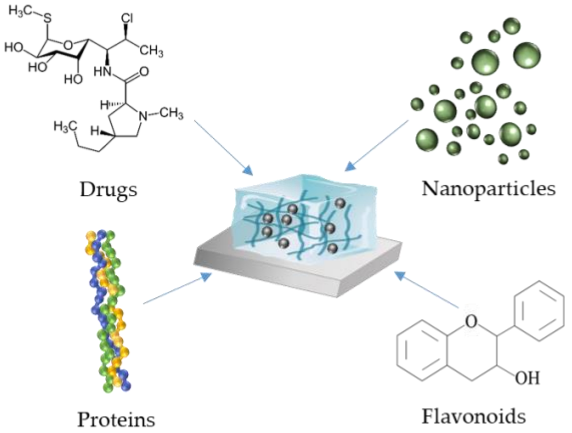


Figure 1: Modifications of composite coatings.

References:

1. Nathanael, A.J., Oh T.H. (2020) Biopolymer Coatings for Biomedical Applications, *Polymers*. 12, 3061.
2. Park, S., Han, U., Choi, D., Hong, J., (2018) Layer-by-layer assembled polymeric thin films as prospective drug delivery carriers: design and applications, *Biomaterials Research*, 22, 29.
3. D'Almeida, M., Attik, N., Amalric, J., Brunon, C., Renaud, F., Abouelleil, H., Toury, B., Grosgogeat, B., (2017) Chitosan coating as an antibacterial surface for biomedical applications, *PLoS one*. 12, e018953.

Biocompatibility assessment of polymer-ceramic composites loaded with plant extract

Dagmara Słota[1], Wioletta Florkiewicz[1], Karina Piętak[1], Aeksandra Szwed[2], Marcin Włodarczyk[2], Małgorzata Siwińska[3], Karolina Rudnicka[2], Agnieszka Sobczak-Kupiec[1]
[1] Department of Materials Science, Faculty of Materials Engineering and Physics, Cracow University of Technology, Krakow, Poland
[2] Department of Immunology and Infectious Biology, Faculty of Biology and Environmental Protection, University of Lodz, Lodz, Poland
[3] Department of Biology of Bacteria, Faculty of Biology and Environmental Protection, University of Lodz, Lodz, Poland

Abstract:

For centuries, naturally derived products have been used for the treatment and prevention of certain diseases. Extracts of many well-known plants are rich in flavonoids, fatty acids, terpenes or terpenoids, thereby demonstrating immunomodulatory and anticancer effects. Moreover, flavonoids reduce the risk of cancer, show beneficial effects on cardiovascular and metabolic health, as well as play an essential role in inflammation, due to which they can reduce the risk of many diseases such as asthma, diabetes and neurodegenerative diseases. Furthermore, many studies have shown that plant metabolites are promising active substances that can be used as bone regeneration enhancers able to promote osteoblast differentiation as well as bone formation.

The presented research involves the biological assay of a biocomposite composed of bioactive hydroxyapatite, a biocompatible polymers such as polyvinylpyrrolidone or sodium aligate and a plant extract. The addition of the plant extract significantly increased the biological value of the material, by giving it new, additional properties. In vitro analysis of cytocompatibility (Figure 1) and immunocompatibility of THP1-Blue NF-κB human monocytes with biocomposites was performed. The obtained satisfactory results suggest the necessity of further research towards the potential use of biomaterials as an intelligent carrier of active substance.

The “Multifunctional biologically active composites for applications in regenerative bone system medicine” project is carried out within the TEAM-NET program of the Foundation for Polish Science financed by the European Union under the European Regional Development Fund. POIR.04.04.00-00-16D7/18.

Keywords: ceramic, polymer, composites, hydroxyapatite, polyvinylpyrrolidone, plant extract

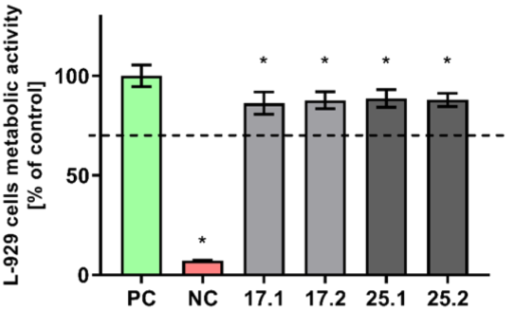


Figure 1: The viability of murine fibroblasts (L-929) after 24 h incubation with biocomposites, evaluated using MTT reduction test according to ISO-10993-5:2009. The positive control (PC) of the viability (100%) consisted of cells incubated without composites. The negative control (NC) of the viability consisted of cells incubated with 0.3% hydrogen peroxide. The dashed line indicates the minimum level (70%) of the cells metabolic activity required to recognize the biomaterial as non-cytotoxic at the in vitro level.

References:

1. Bellavia, D., Dimarco, E., Costa, V., Carina, V., De Luca, A., Raimondi, L., Fini, M., Gentile, C., Caradonna, F., Giavaresi, G. (2021) Flavonoids in Bone Erosive Diseases: Perspectives in Osteoporosis Treatment, *Trends in Endocrinology & Metabolism*, 32(2) 76-94.
2. Soundarya, S.P., Sanjay, V., Haritha Menon, A., Dhivya S., Selvamurugan N. (2018), Effects of flavonoids incorporated biological macromolecules based scaffolds in bone tissue engineering, *International Journal of Biological Macromolecules* 110, 74-87.

Tuning the size, shape and pore structure of mesoporous silica nanoparticles

M. Llenas [1,*], S. Sandoval [1], C. Martínez [1], M. Florensa [1], G. Tobias [1]
[1] Solid State Chemistry, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Bellaterra, Spain

Abstract:
Mesoporous silica nanoparticles (MSN) have been widely used in recent decades due to their unique properties, such as controllable size, shape and porosity, ordered pore structure, very high specific surface area and good chemical stability, making them attractive for a variety of applications such as catalysis, separation processes or sensing. In addition, MSN also present important biocompatibility, high loading capacity and ease of functionalization making them gain a tremendous attention as drug delivery systems. As novel platforms for biomedical application, the control of their physicochemical properties is extremely important as they play a key role in the biodistribution and tissue accumulation of these nanoparticles. In the present work, MSN with different properties have been prepared by fine control of the synthesis parameters; namely, the precursors and their ratios, the reaction time, temperature and type of agitation. The obtained nanoparticles have been characterized by complementary techniques, including electronic microscopy, spectroscopy, thermal analyses and adsorption studies. Particles with different size, morphology and pore size and structure have been obtained thus shedding light on how the selected synthetic approach and employed conditions modify the MSN properties, highly relevant for the targeted biomedical application.

Keywords: mesoporous silica nanoparticles, silica-based nanomaterials, biomedical applications.

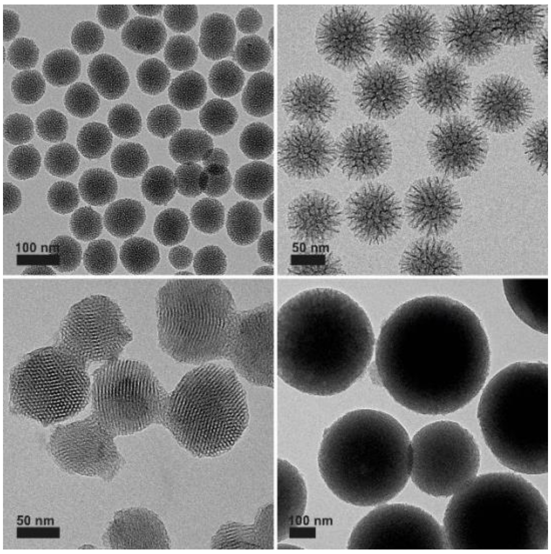


Figure 1: Images illustrating different types of nano-particles regarding the particle size, pore size and structure.

Redox-Sensitive Core-Multishell Nanocarrier Systems

K. Rajes [1,*], K. A. Walker [1], S. Hadam [2], F. Zabihi [1,2], J. Ibrahim-Bacha [1], G. Germer [1], P. Patoka [1], B. Wassermann [1], F. Rancan [2], E. Rühl [1], A. Vogt [2], R. Haag [1]
[1] Department of Biology, Chemistry, and Pharmacy, Freie Universität Berlin, Berlin, Germany
[2] Department of Dermatology and Allergy, Charité - Universitätsmedizin Berlin, Berlin, Germany

Abstract:
Drug delivery into and across the skin has wide applications ranging from conventional dermatological therapy of inflammatory skin diseases, such as atopic dermatitis or psoriasis, and skin tumour therapy, such as topical chemotherapy and photodynamic therapy, to transcutaneous drug delivery and vaccination. While systemic therapy experienced a surge of innovations and new active molecules in the past decade, only few innovative molecules made it into new topical formulations due to poor skin uptake.

Dermal drug delivery can host problems due to various reasons such as a drug's lipophilicity or size affecting its permeability through the skin barrier. Skin is characterised by different redox environments changing over the different skin layers. Those redox environments also vary in healthy and inflamed skin, thus offering the usage of redox dependent drug delivery.

Polymeric drug delivery systems aim at overcoming the solubility issue by entrapping the drug in a solubility-enhancing polymeric environment. Among the vast diversity of polymeric drug delivery systems, dendritic nanocarriers are considered as universal systems, as their defined core-shell architecture offers many benefits.

The skin harbours mainly glutathione (GSH) / glutathione disulphide (GSSG) buffers maintaining the redox systems. Oxidative environments host among increased GSSG levels also reactive oxygen species (ROS). Carrier systems can utilise those redox environments by incorporating reduction as well as oxidation sensitive components. Hydrophobicity changes of thioether moieties upon oxidation can thereby lead to a controlled drug release in the skin while reduction of sulphide bonds can lead to its cleavage and subsequently drug release.

An *ex vivo* skin-based inflammatory model enabled to study both drug dermal delivery and anti-inflammatory efficacy. Rapamycin formulated in CMS nanocarriers thereby efficiently reduced the expression of inflammatory cytokines IL-2 in Jurkat T cells.

Keywords: drug delivery, nanocarriers, core-multishell systems, redox-responsiveness, inflammation, dermal drug uptake, rapamycin, biomedical applications.

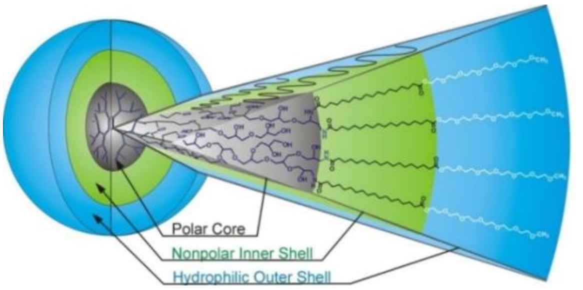


Figure 1: Figure illustrating the structure of core-multishell nanocarrier systems with a hydrophilic core and outer shell while the hydrophobic inner shell contains the drug and can be oxidatively stimulated for release.

References:

1. Xiao, C., Ding, J., Ma, L., Yang, C., Zhuang, X., Chen, X. (2015), Synthesis of thermal and oxidation dual responsive polymers for reactive oxygen species (ROS)-triggered drug release, *Polym. Chem.*, 6, 738–747.
2. Ding, J., Chen, J., Li, D., Xiao, C., Zhang, J., He, C., Zhuang, X., Chen, X. (2013), Biocompatible reduction-responsive polypeptide micelles as nanocarriers for enhanced chemotherapy efficacy in vitro., *J. Mater. Chem. B*, 1, 69–81.

Functionalization of harmonic nanoparticles for multimodal imaging and theranostic applications.

Adrian Gheata [a,*], Raphaël De Matos [a], Jérémy Vuilleumier [a], Geoffrey Gaulier [b], Gabriel Campargue [b], Luigi Bonacina [b], Davide Staedler [c], Dario Diviani [c], and Sandrine Gerber-Lemaire [a]

a) Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
b) GAP-Biophotonics, University of Geneva, CH-1211 Geneva, Switzerland
c) Department of Biomedical Sciences, University of Lausanne, CH-1011 Lausanne, Switzerland
*email: adrian.gheata@epfl.ch

Abstract:

Cancer is among the leading causes of death worldwide, and as knowledge of the disease continues to grow there is an increasing interest towards precision medicine: more specifically towards the theranostics field, i.e the development of targeted molecular probes combining specific diagnosis and treatment modalities. The theranostic paradigm involves merging, in a single agent, specific tumor biomarker targeting, multimodal imaging techniques which allow to overcome the inherent limitations of classical methods, and the controlled delivery of anticancer compounds. This strategy thus aims at high diagnosis sensitivity for earlier tumor detection and the reduction of off-target effects, which are critical factors in patient survival rates. In this context, inorganic nanoparticles emerge as promising tools owing to their surface properties, which are amenable to post-functionalization, and their imaging properties. [1,2]

This project aims at developing such multimodal theranostic tools based on harmonic nanoparticle (HNP) materials. These metal oxide nanomaterials, characterized by a crystalline structure lacking inversion symmetry (e.g $LiNbO_3$, LNO), exhibit a non-linear optical response by generating second- and third-harmonic signals upon laser excitation. [3] A silica-based coating layer allows for improved biocompatibility of the inorganic HNPs and for the introduction of surface azide moieties, which were exploited for subsequent functionalization through bioorthogonal copper-free click reaction with cyclooctyne-modified ligands, [4] or standard copper-catalyzed click chemistry with alkyne-modified ligands. An erlotinib analogue (ELA) was chosen for therapeutic effect on neoplastic cells overexpressing the Epidermal Growth Factor Receptor (EGFR). [5] In addition, the HNPs were covalently conjugated to a lanthanide (III) chelate, potentially acting as an MRI/X-ray contrast agent or a luminescent probe depending on the selected lanthanide atom, paving the way for multimodal imaging. Light-sensitive drug carriers were produced by the grafting of chemotherapeutics to the surface of HNPs through photosensitive tethers based on coumarinyl moieties. [6] Irradiation of the HNPs with near-infrared (NIR) light allowed switching between imaging and treatment modalities by tuning of the excitation energy. Excitation at high wavelengths (> 1000 nm) is used for multi-harmonic detection, while lower wavelengths (~800 nm) results in the harmonic emission of ultraviolet light, inducing cleavage of the phototrigger and release of the therapeutic cargo. An erlotinib derivative caged to the surface of silica-coated LNO nanoparticles was released by NIR irradiation *in vitro* against EGFR+ DU-145 human androgen independent prostate cancer cells, and showed successful cell growth inhibition.

Keywords: Photosensitive tether, harmonic nanoparticles, light-triggered uncaging, surface functionalization.

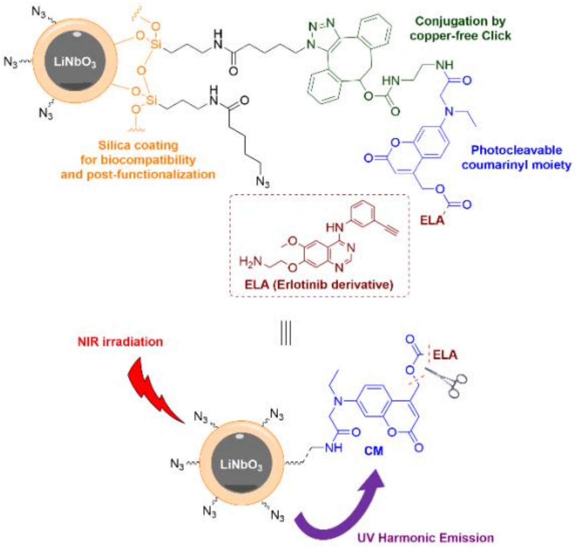


Figure 1: Controlled uncaging of therapeutic compound triggered by the harmonic emission of functionalized LNO HNPs.

References:

1. Chen, H., Zhang, W., Zhu, G., Xie, J., & Chen, X. (2017). Rethinking cancer nanotheranostics. *Nature Reviews Materials*, 2(7), 1-18.
2. Liu, M., Anderson, R. C., Lan, X., Conti, P. S., & Chen, K. (2019). Recent advances in the development of nanoparticles for multimodality imaging and therapy of cancer. *Medicinal research reviews*.
3. Bonacina, L. (2013). Nonlinear nanomedecine: harmonic nanoparticles toward targeted diagnosis and therapy. *Molecular Pharmaceutics*, 10(3), 783-792.
4. Staedler, D., Passemard, S., Magouroux, T., Rogov, A., Maguire, C. M., Mohamed, B. M., ... & Mugnier, Y. (2015). Cellular uptake and biocompatibility of bismuth ferrite harmonic advanced nanoparticles. *Nanomedicine: Nanotechnology, Biology and Medicine*, 11(4), 815-824.
5. Cataldo, V. D., Gibbons, D. L., Pérez-Soler, R., & Quintás-Cardama, A. (2011). Treatment of non–small-cell lung cancer with erlotinib or gefitinib. *New England Journal of Medicine*, 364(10), 947-955.
6. Vuilleumier, J., Gaulier, G., De Matos, R., Ortiz, D., Menin, L., Campargue, G., ... & Bonacina, L. (2019). Two-Photon-Triggered Photorelease of Caged Compounds from Multifunctional Harmonic Nanoparticles. *ACS applied materials & interfaces*, 11(30), 27443-27452.

Synthesis and characterization of multifunctional iron-doped ZnO nanoparticles for anti-tumoral applications

November 2019
| https://doi.org/10.3389/fbioe.2019.00374

M. Carofiglio [1*], M. Laurenti [1], L. Racca [1], S. Barui [1], N. Garino [1], V. Cauda [1]
[1] Department of Applied Science and Technology, Politecnico di Torino, Turin, Italy

Abstract:

Pancreatic ductal adenocarcinoma (PDAC) is one of the most devastating diseases for which limited benefits are obtained by current therapeutics. Therefore, novel therapeutic and early diagnostic techniques are required to address this tumor.

Zinc oxide nanoparticles (ZnO NPs) are gaining interest in nanomedicine, due to their high versatility and properties, which can be easily tailored by means of various strategies. Doping is among the most promising ones: the introduction of ions coming from different elements may induce new potentialities to ZnO NPs [1] which can be exploited to design a novel theranostic nanoparticle. Here iron-doped ZnO NPs (Fe:ZnO NPs) functionalized with amino-propyl groups and oleic acid are synthesized to obtain a multipurpose theranostic nanomaterial: on the one hand, Fe doping induces magnetic responsiveness with potential applications as contrast agent in magnetic resonance imaging (MRI); on the other hand the amino-functionalized ZnO NPs are able to generate reactive oxygen species (ROS) under ultrasound (US) activation, aiming at pancreatic cancer cells killing.

Fe:ZnO NPs were synthesized with different iron concentrations (0, 6, 12 at.%) with an oleic acid shielding by a wet chemical method, while the amino group functionalization was obtained with a post-synthetic grafting approach [2] and exploited for dye labelling. The particles were characterized with scanning electron microscopy, revealing spherical 8 nm NPs. Energy Dispersive X-ray Spectroscopy (EDS) was used to assess the actual doping level of the NPs (0, 4.8 and 7.8 at.%), while Fourier transform infrared spectroscopy (FTIR) confirmed their functionalization with both oleic acid and amino groups. Moreover, doping with iron was revealed to be effective, with concentration dependence, in increasing the paramagnetic signals obtained in DC magnetization measurements, as well as the generation of reactive oxygen species under ultrasound stimulation (Figure 1). In addition, Fe:ZnO NPs showed to be safe up to 20 µg/mL concentration and no significant cell viability reduction was found at this concentration, considering the different levels of doping. Nanoparticles uptake experiments were used to assess the number of NPs that could contribute to intracellular reactive oxygen species generation upon US stimulation, establishing that a high percentage of cells have internalized the NPs with a fast internalization rate.

Keywords: Zinc Oxide, reactive oxygen species, magnetic resonance imaging, ultrasound, nanoparticles.

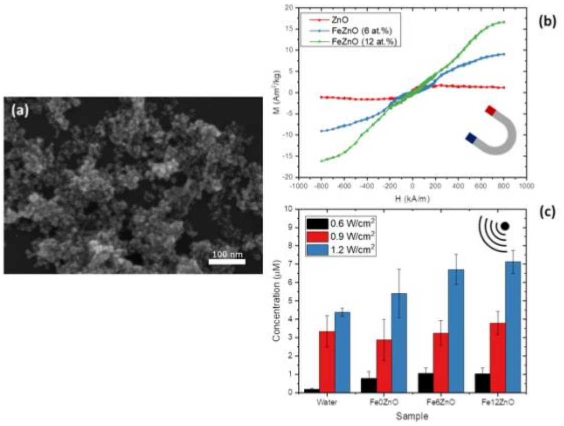


Figure 1: (a) FESEM, (b) magnetic properties and (c) ROS generation under US stimulation characterization of iron-doped ZnO nanoparticles.

References:

1. Carofiglio M., Barui S., Cauda V., Laurenti M. Doped zinc oxide nanoparticles: synthesis, characterization and potential use in nanomedicine *Applied Sciences*, 2020, Vol. 10(15), pp. 5194, EISSN 2076-3417, doi: 10.3390/app10155194
2. Barui S., Gerbaldo R., Garino N. Brescia R., Laviano F., Cauda V. Facile chemical synthesis of doped ZnO nanocrystals exploiting oleic acid *Nanomaterials* 2020, 10(6), 1150; doi: 10.3390/nano10061150
3. Vighetto V., Ancona A., Racca R. Limongi T., Troia A., Canavese G., Cauda V. The synergistic effect of nanocrystals combined with ultrasound in the generation of reactive oxygen species for biomedical applications *Front. Bioeng. Biotechnol.*, vol. 7. 26 November 2019 | https://doi.org/10.3389/fbioe.2019.00374

Developing doped ZnO-based immunocompatible tumor targeted nanotheranostics to improve pancreatic cancer treatment

S. Barui[1]*, N.M. Percivalle[1], M. Conte[1], B. Dumontel[1], L. Racca[1], M. Carofiglio[1], V. Cauda[1]
[1] Department of Applied Science and Technology, Politecnico di Torino, Turin, Italy

Abstract:

Despite different nanomaterials were developed so far in particular against cancer, very little attention is paid to their potential immunogenicity, to their final destiny, as well as to the importance of zero-delivery in unwanted places. Thus, there is still a huge disproportion between the present nanomedicine tools and the clinical requirements. Moreover, in the clinical management of cancer patients, the timely assessment of therapeutic response to a given therapy is critical for making treatment decisions. Herein, to address these important challenges we aim to develop a novel theranostic immunocompatible tumor targeted nanoconstructs to enhance intracellular release of the drugs to cancer cells and provide contrast enhancement for treatment monitoring, especially in pancreatic cancer, one of the most lethal human malignancies till date.

Zinc oxide nanocrystals (ZnO-NCs) have shown great potential application *in vitro* as well as *in vivo* for targeted therapy due to its biocompatibility and pH-sensitivity to assure effective endosomal drug release. Likewise, ZnO-NCs doped with rare earth elements can be probed for magnetic resonance imaging (MRI) which helps to easy detect drug-loaded nanoparticles in pancreatic tumor located deep in the retroperitoneal cavity [1]. Therefore, we synthesized Gd-doped ZnO-NCs as theranostic vehicle and introduced a phospholipidic coating based on lipids derived from autologous extracellular vesicles (EVs) as biomimetic shell to limit the aggregation of NCs in biological media and address the potential immunogenicity and biocompatibility. Targeting was then accomplished by functional peptides (e.g., pancreatic pathological microenvironment homing CKAAKN peptide), able to direct the drug-loaded nanoconstruct to the right site of action (Figure 1).

The co-precipitation method was used to synthesize and control the doping of ZnO:Gd in NCs [2]. Gemcitabine, the baseline drug of pancreatic cancer treatment, was successfully adsorbed on the surface of NCs in a good amount. The freeze thaw technique was exploited to prepare novel multifunctional lipid-coated nanoconstruct by coupling the Gemcitabine-loaded doped ZnO-NCs with lipidic bilayers derived from EVs. The size (140-150 nm) and shape (spherical) of nanoconstructs were characterized by Dynamic Light Scattering, Nanoparticle Tracking Analysis and Transmission Electron Microscopy. Energy Dispersive X-Ray for elemental analysis and DC magnetometry to determine MRI applicability of the nanoconstructs were also performed. Flow cytometric analysis of cell internalization in pancreatic cancer cells (e.g., BxPC-3) showed potential advantage of introducing target peptide ligand in the nanoconstruct. Cellular cytotoxicity assay in BxPC-3 cells dictated >20% increased cell killing efficacy of Gemcitabine when delivered through the nanoconstruct than as free drug. Taken together, our designed theranostic EV-coated doped ZnO-NCs can have a significant impact on the standard treatment of pancreatic cancer.

Keywords: Doped Zinc Oxide nanocrystal, Extracellular vesicle, Targeted Nanotheranostics, Pancreatic cancer, Magnetic resonance imaging.

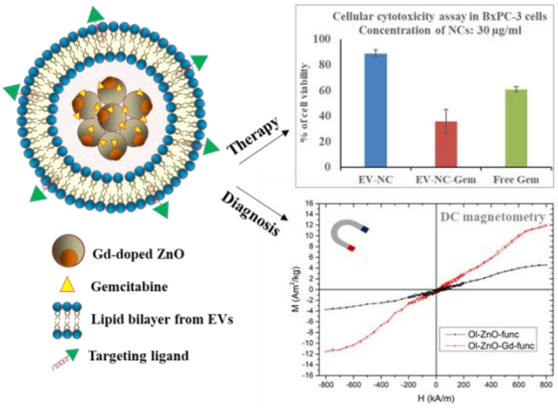


Figure 1: Multifunctionalized immunocompatible targeted novel nanotheranostics in pancreatic cancer (therapy as well diagnosis)

References:

1. Carofiglio, M., Barui, S., *et al.* (2020), Doped zinc oxide nanoparticles: synthesis, characterization and potential use in nanomedicine, *Applied Sciences*, 10, 5194.
2. Barui, S., *et al.* (2020), Facile chemical synthesis of doped ZnO nanocrystals exploiting Oleic acid, *Nanomaterials* 10, 1150.

Investigation of the anticancer effects of ZnO nanocrystals remotely activated

L.Racca [1,2,*], V. Cauda [1,2]

[1] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy

Abstract:

Cancer is the second cause of death worldwide, with 18.1 million new cancer cases and 9.6 million cancer-related deaths only in 2018.

Several nanomaterials have been proposed alone, or in combination with a second agent, i.e. chemotherapy, to fight cancer cells. In this field, an attractive proposal is the use of nanoparticles that work in synergy with an external physical stimulation, as light or ultrasound, able to trigger their cytotoxic potential, and thus confining the toxic outcomes only in a target site to prevent the development of side effects. Different physical inputs have been proposed for this purpose in the last years, as depicted in Figure 1. However, the use of ultrasound and shock waves is particularly attractive due to their already use in clinical practice and low cost materials, the focusing capability. The shock waves treatment in particular is also associated by a reduced increment of the temperature in comparison with ultrasound one, leading the evaluation the non-thermal effects of the acoustic cavitation, that are retained to be widely involved in the activation of molecules and nanoparticles. Here in particular we synthetized zinc oxide nanocrystals (ZnO NCs) and evaluated their effect on cancer cells alone, in particular cytotoxicity and internalization. Further we exposed cancer cells pre-treated with ZnO NCs to a remote physical stimulation trying to find the optimal parameters to trigger the synergism between ZnO NCs and the stimulus and achieve cancer cell death.

Keywords: remotely-activated nanoparticles, zinc oxide nanoparticles, ultrasound, shock waves, acoustic cavitation, cancer therapy.

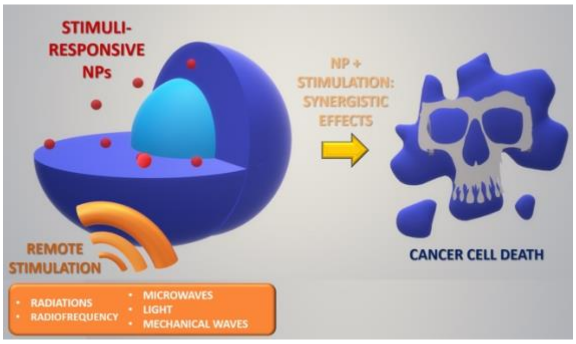


Figure 1: Figure summarizing the principles of remotely-activated nanoparticles. A nanoparticles could be associated to one or more physical stimulations, and their synergistic action is able to enhance cancer cell death.

References:

1. International Agency for Research in Cancer (2018), Latest Global Cancer Data, World Health Organization, Geneva,
2. Racca, L.; Cauda, V. (2020), Remotely Activated Nanoparticles for Anticancer Therapy. *Nano-Micro Lett*. 13, 11,

Protein-stabilized amorphous Titania Nanoparticles for Sonodynamic Therapy

V.Vighetto [1*], L. Racca [1], M. Canta [1], Joana C. Matos [2,3,4], M. Clara Gonçalves [2,4], V. A. Cauda [1]

[1] Department of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Turin, Italy
[2] Centro de Química Estrutural, Universidade de Lisboa, Av. Rovisco Pais, IST, 1000 Lisboa, Portugal;
[3] Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, 2685-066 Bobadela LRS, Portugal;
[4] Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1000 Lisboa, Portugal

Abstract: Stimuli-responsive nanoparticles (NPs) are getting increasingly relevant as therapies to treat cancer. NPs with specific chemical composition and/or structure are studied in combination with external stimuli (magnetic, light or ultrasounds), creating new and more advanced tools. Amorphous titania (a-TiO_2) nanoparticles (NPs) present very interesting characteristics, as photo- reactivity and stability, and effective bactericidal properties[1]. Their production is inexpensive and they are non-toxic. Both pristine a-TiO_2 and propylamine- functionalized a-TiO_2-NH_2 NPs, are synthetized through a novel, room-temperature and base-catalyzed, sol-gel method. Here they are presented for ROS generation and as an enhancer of acoustic inertial cavitation. Their behaviour was evaluated under different acoustic wave irradiations and in presence or absence of propylamine groups.[2] To further improve colloidal stabily in biological fluids a-TiO_2-NH_2 NPs were coated with bovine serum albumin (BSA). Protein-stabilized amorphous-titania NPs showed no cancer cell cytotoxicity. The cytotoxic effects were also investigated in combination with acoustic external stimulus. A systematic study, combining the BSA-coated amorphous titania NPs and shock waves in *in vitro* cell culture was performed at different NPs concentrations, different time steps and single *versus* multiple treatments.

Keywords: nanotechnology, silica nanoparticles, ammino-funcionalization, ultrasound, shock wave, biomedic al applications.

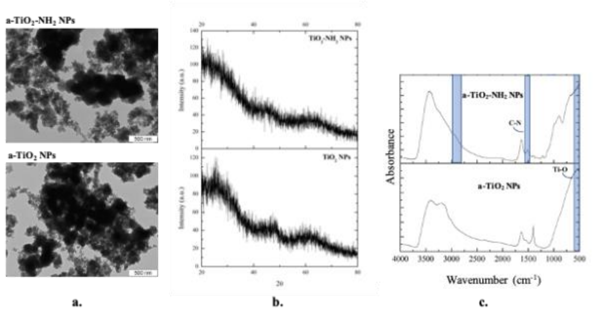


Figure 1: Figure illustrating hysical characterization of amorphous TiO_2 (a-TiO_2) (lower panels) and a-TiO_2-NH_2 nanoparticles (NPs) (upper panels): (**a**) TEM images, (**b**) X-ray diffractograms, and (**c**) FTIR spectra.

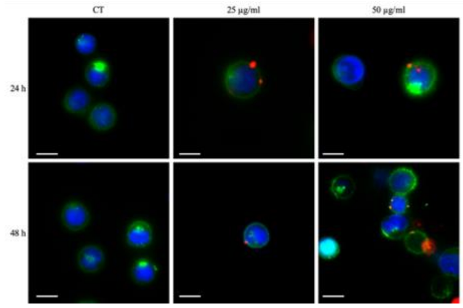


Figure 2: Fluorescence microscopy images of Daudi cells treated with different concentrations (25 µg/mL and 50 µg/mL) of TiO_2-NH_2/BSA NPs after 24 h and 48 h of incubation..

References:

1. Matos, J. C., Oliveira, C. & Gonçalves, M. C. Daylight Bactericidal Titania Textiles: A Contribution to Nosocomial Infections Control. *Molecules* **24**, 1891 (2019).
2. Matos, J. C. *et al.* Biomimetic Amorphous Titania Nanoparticles as Ultrasound Responding Agents to Improve Cavitation and ROS Production for Sonodynamic Therapy. *Appl. Sci.* **10**, 8479 (2020).

In vitro evaluation of biomimetic nanoparticles for liver cancer treatment

M. J. Bigaj-Józefowska [1*], E. L. Coy [1], M. Grabowska [2], S. Jurga [1], B. F. Grześkowiak [1]
[1] NanoBioMedical Centre, Adam Mickiewicz University, Poznań, Poland
[2] Institute of Bioorganic Chemistry, Polish Academy of Sciences, Poznań, Poland

Abstract:

Cancer treatment has been a focus of research for many years. With the advancement of nanotechnology, nanoparticles have become one of the mainstream research efforts to improve the safety and effectiveness of traditional cancer therapies. The primal role of the nanocarriers is to overcome limitations of the anticancer drugs such as lack of selectivity, poor solubility, early clearance from the bloodstream. An ideally designed drug delivery system (DDS) is responsible not only for the targeted delivery of the chemotherapeutic agent to the tumor and protecting the substances against early immune recognition. The appropriate choice of carrier material can provide such a system with additional therapeutic functionalities and imaging.

The subject of our study is a DDS based on porous polydopamine (PDA) nanoparticles. PDA is a material known for its biosafety, easy functionalization, and photothermal properties when irradiated with a NIR laser. By loading the nanoparticles with the drug doxorubicin, we obtain a system capable of synergistic anticancer therapy. Membranes isolated from the HepG2 cancer cells were used to coat the nanocarriers. Successful translocation of natural membrane proteins to the surface of nanoparticles provides the system with the properties of homotypic targeting to cells of the same type. The investigated nanoformulations were thoroughly characterized for their physio-chemical properties and drug loading and release in various pH conditions and under NIR laser irradiation. Optimization of the coating process led to obtaining core-shell structures with the confirmed presence of membrane proteins (Figure 1). Moreover, the *in vitro* cytotoxicity assays confirmed potential of the PDA@DOX@Mem NPs as agents in the targeted treatment of hepatocellular carcinoma.

Keywords: biomimetic nanoparticles, cancer therapy, hepatocellular carcinoma, PDA, biomedical applications.

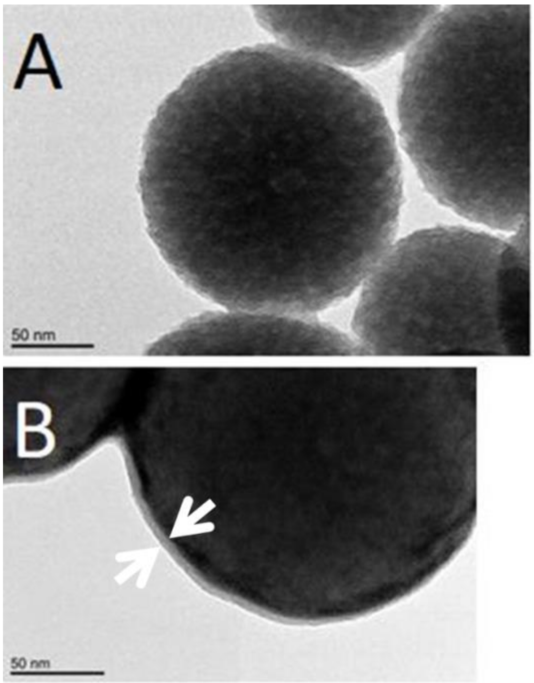


Figure 1: TEM images of porous PDA NPs (A) and HepG2 membrane-coated porous PDA NPs (B). The width of the membrane (indicated by arrows) is between 6 and 7 nm.

Acknowledgements:

The research was financed by The National Science Centre (NCN), Poland, under project number UMO-2018/31/D/ST8/02434.

References:

1. Li, Anning et al. 2021. “Recent Advances of Biomimetic Nano-Systems in the Diagnosis and Treatment of Tumor.” *Asian Journal of Pharmaceutical Sciences* 16(2): 161–74.
2. Mrówczyński, Radosław. 2018. “Polydopamine-Based Multifunctional (Nano)Materials for Cancer Therapy.” *ACS Applied Materials & Interfaces* 10(9): 7541–61.
3. Sun, Huiping et al. 2016. “Cancer-Cell-Biomimetic Nanoparticles for Targeted Therapy of Homotypic Tumors.” *Advanced Materials* 28(43): 9581–88.

Development of Multifunctional Nanocarriers Based on PAMAM Dendrimers for Gene/drug co-delivery for Targeted Colorectal Cancer Therapy

B. Bulkurcuoğlu [1,2], MU Gurbuz[3], K. Pavlov[4], S. Tyciakova[4] , M Matuskova[4], M Tulu[3*], S Ercelen[1*]
[1] TUBITAK MRC Genetic Engineering and Biotechnology Institute, Kocaeli, Turkey
[2] Biotechnology Institute, Gebze Technical University, Kocaeli, Turkey
[3]Department of Chemisty, Yıldız Technical University, İstanbul, Turkey
[4]Cancer Research Institute, Biomedical Research Center SAS, Bratislava, Slovak Republic

Abstract:

Colorectal cancer (CRC) is the third leading cause of cancer-related deaths in the world [1]. Despite many therapeutic opportunities, prognosis remains dismal for patients with metastatic disease (mCRC) and %40 of early-stage patients develop recurrence after chemotherapy and %90 of patients with metastatic cancer develop multidrug resistance [2]. Nanomedicine due to its promise in providing superior therapeutic benefits is increasingly used in clinical practice. Development of multifunctional nanocarriers enables targeted co-delivery of drugs and genes, while maintaining their chemo-physical properties and biological functions. Dendritic polymers are highly branched polymers with controllable structures, which possess a large population of terminal functional groups, low solution or melt viscosity, and good solubility. These properties allow their use in numerous bio applications, including gene, drug, and protein delivery, bioimaging, tissue engineering etc. Uniform distribution, stability and multifunctionality of dendrimers accelerated their application in targeted anti-tumour therapies as a nanomedicine [3]. In the present study a multifunctional nanotherapeutic system based on polyamidoamine (PAMAM) dendrimers for targeted co-delivery of 5-fluorouracil (5FU), plasmid DNA (containing apoptosis-mediating TRAIL gene) and selective targeting moiety (folate, FA) were synthesized to increase the efficacy of colon cancer treatment and to overcome drug resistance.

Dendrimer conjugates were successful in complexation with model DNA and forming stable and small sized complexes. It protects DNA from nuclease degredation. Cytotoxicity of dendrimer conjugates is quite low and preliminary transfection results with HCT-116 cell line were prospective as a novel multifunctional nanocarrier for synergistic targeted cancer therapy.

Keywords: Drug delivery, gene delivery, PAMAM dendrimer, multifunctional nanocarrier, co-delivery, nanomedicine, cancer therapy.

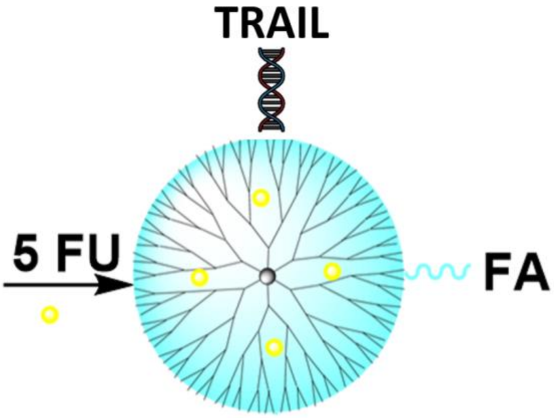


Figure 1: Design of novel multifunctional nanotherapeutic.

References:

1. Keum N, Giovannucci E. Global burden of colorectal cancer: emerging trends, risk factors and prevention strategies. Nat Rev Gastroenterol Hepatol. Springer Science and Business Media LLC. 2019;16(12):713–732.
2. Qian D, Li ZP, Huang CM, Zhen L, Tang QL. Effect and mechanism of DNMT inhibitor on the reversal of multidrug resistance in human colon cancer cell line sw620/L-OHP. J Sichuan Univ. 2010;41(6):975–979.
3. Kesharwani, P., & Iyer, A. K. (2015). Recent advances in dendrimer-based nanovectors for tumor-targeted drug and gene delivery. *Drug Discovery Today*, *20*(5), 536–547. https://doi.org/10.1016/j.drudis.2014.12.012

Simple design of antibody-based microarrays via DNA-directed immobilization in multiplex diagnostics of viral infections

S. Karoń [1,2], M. Drozd [1,2], E. Malinowska [1,2]

[1] Faculty of Chemistry, The Chair of Medical Biotechnology, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
[2] Center for Advanced Materials and Technologies, Warsaw University of Technology, Poleczki 19, 02-822 Warsaw, Poland

Abstract:

Viral ability of fast adaptation and spreading has led to the biggest health struggle of the world in the past 100 years – outbreak of pandemic. Therefore, reliable immunodiagnostics of viral infections and immunological methods which enable rapid adjustment and development of receptor layers for detection of the viral biomarkers are crucial in the case of future needs. The aim of the current study is to design microarray for diagnostics and profiling of human response to viral infections. It is based on "click biology"-type immobilization (Figure 1.). The viral antigens or antibodies against them are conjugated with DNA oligos (ssDNA anchors), purified through ionic chromatography and immobilized on the gold surface covered with complimentary sequences. SPR and SPRi measurements were conducted for multiplex detection of several viral infection biomarkers. Effective immobilization enabled characterization of interactions between the antigens and specific antibodies. In the future studies the implementation of the designed immunosensing layer for microarray construction will be possible. This approach is interesting due to the effective immobilization and reversible rearrangement of the receptor layer which allows for its easy customization. Moreover, obtained immunosurfaces are applicable in other types of biosensors, they enable functionalization of macroscopic transducers and nanomaterials for bioanalytical applications. DNA-directed immobilization is a good start for the construction of multiplex and versatile microarrays and it is worth further development.

Keywords: DNA-directed immobilization, biosensor, microarray, viral multiplex immunodiagnostics, SPR, profiling

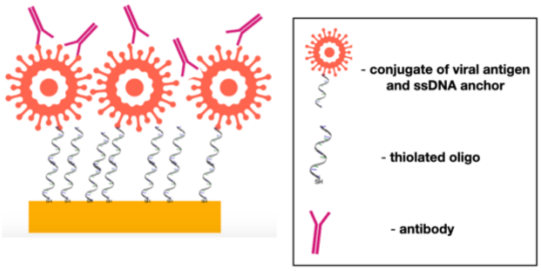


Figure 1: Figure illustrating gold chip for SPR and SPRi measurements covered with thiolated oligos complimentary to ssDNA anchors conjugated with viral antigens.

References:

1. Choi, J. H., Lee, J. H., Son, J. & Choi, J. W. Noble metal-assisted surface plasmon resonance immunosensors. *Sensors (Switzerland)* **20**, (2020).
2. Jiang, H. *et al.* SARS-CoV-2 proteome microarray for global profiling of COVID-19 specific IgG and IgM responses. *Nat. Commun.* **11**, (2020).

This research is supported by the ImGen "Opracowanie konstrukcji i technologii wytwarzania miniaturowych urządzeń diagnostycznych do szybkiego wykrywania wirusa SARS-CoV-2 w trybie POCT"; project is funded by the National Centre for Research and Development in Poland (grant no. POIR.01.01.01-00-0638/20). More information about the ImGen project is available on the webpage https://cezamat.eu/projekty/w-toku/imgen/

Magnetically Induced Cargo Release Inside Living Cells

Leroy M. Nack[a,*], Zhang Li[a], Dingcheng Zhu[a], Wolfgang J. Parak[a,b]
[a] Fachbereich Physik, CHyN, Universität Hamburg, Hamburg, Germany
[b] Fachbereich Chemie, Universität Hamburg, Hamburg, Germany
*Corresponding author. E-Mail: LeroyM.Nack@outlook.de

Abstract:

Controlled opening of polyelectrolyte capsules by external stimuli has already been extensively studied during the past years, especially in the field of targeted drug delivery. Compared to well-investigated laser triggered opening, alternating magnetic fields (AMFs) can penetrate more deeply into thick biological samples without causing damage due to significantly reduced absorption.[1,2]

Given various magnetic nanoparticles, developed as heat-mediators for hyperthermia therapy, their usability for magnetic opening of capsules inside living cells is rarely reported. Herein, we initially developed sufficiently openable polyelectrolyte microcapsules, functionalized by embedding various iron oxide-based magnetic nanoparticles (IONPs) into the shell. To achieve high heat-generation efficiency, IONPs with different compositions were prepared and analysed. The best ones with extremely high specific absorption rate (SAR) values up to more than 1000 W/g were integrated into the polymer shell of the microcapsules. We then successfully induced irradiation-controlled release of the encapsulated cargo inside cancer cells under application of alternating magnetic fields (AMF). To visualize the cargo release, the capsules were loaded with a highly fluorescent probe (for instance calcein) and incubated with different cell lines to induce uptake. Upon AMF irradiation, the IONPs locally transformed electromagnetic energy into heat, enabling shell destruction and resulting in rapid release of probe into the cytosol, without harming the cells. This process could be observed on a large scale for a multitude of cells simultaneously but also for individual ones by examination of a specific cell before and after irradiation.

This work demonstrates that magnetically induced cargo delivery inside living cells is practicable. It represents a non-invasive and effective method. However, it remains mandatory to finely tune field and particle parameters to avoid damage and achieve desired release.

References

1. S. Carregal-Romero *et al.*, Nanoscale 7, 570-576 (2015).
2. D. Zhu *et al.*, Advanced Drug Delivery Reviews 138, 117-132.

Delivery of Macromolecular Drugs via Coated Silica Particles

Y. Brasse[1,*], A. Colbus[1], I. Tavernaro[2], A. Kraegeloh[1]
[1] Program Division Nano Cell Interactions, Leibniz Institute for New Materials, Saarbrücken, Germany
[2] Bundesanstalt für Materialforschung und –prüfung (BAM), Fachbereich 1.2 Biophotonik, Berlin, Germany

Abstract:

Drug-eluting implants feature favorable healing properties by local delivery of pharmaceuticals. Their controlled release is a major challenge in the design of drug-eluting devices such as stents, tissue scaffolds, or wound dressings.[1] We discuss the benefit of silica nanoparticle based systems for the controlled release of macromolecular therapeutics.

A core feature of delivery systems for medical applications is the biocompatibility of the carrier itself. Amorphous silica (SiO_2) particles possess the required low toxicity and are thus approved for use in food and drugs.[2,3] Wet-chemical synthesis allows for precise control of the particle size, morphology and porosity. Hereby, the cellular uptake of nanoparticles and containing drugs can be tailored.[4] The surface functionalization of silica particles can be tuned by simple silane chemistry which enables further modification and synthesis of core-shell particles.[5]

Here, we demonstrate the preparation and cellular uptake of drug-coated silica nanoparticles. By applying particles with sizes below 100 nm, these can be internalized efficiently by the surrounding cells.[6] Fluorescence labeled model drugs were localized on the particles and within cells by fluorescence microsopy. We compare their release, depending on different parameters such as pH and ionic strength. It is proposed that the drug is released and the particles are degraded by dissolution within the cells.[7]

Keywords: silica particles, drug-coated nanoparticles, particle dissolution, controlled release

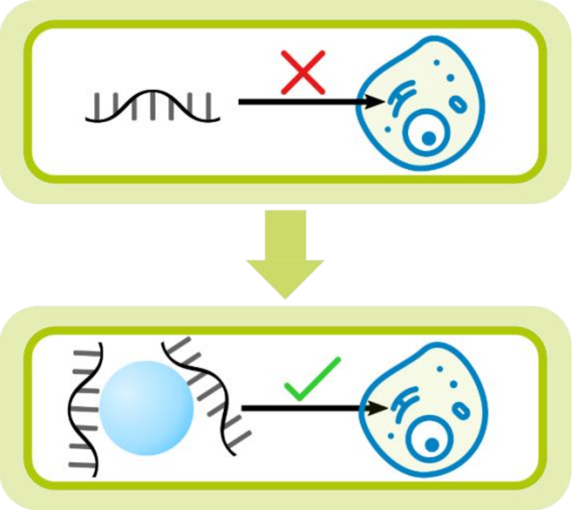


Figure 1: Schematic depiction of cellular uptake for macromolecular drugs. Top: pure drugs are poorly absorbed. Bottom: Drug coated silica particles are eailily internalized by cells.

References:

1. Zilberman, M., Kraitzer, A., Grinberg, O., Elsner, J.J. (2010) Drug-Eluting Medical Implants. In: Schäfer-Korting M. (eds) Drug Delivery. Handbook of Experimental Pharmacology, vol 197. Springer, Berlin, Heidelberg.
2. Regulation (EC) No 1333/2008 of the European parliament and of the council (16 December 2008), Annex II. Accessed via https://eur-lex.europa.eu/ on 15.06.2021.
3. Inactive Ingredient Search for Approved Drug Products, search results for ‘silicon dioxide’ via https://www.accessdata.fda.gov/ scripts/cder/iig/index.cfm on 15.06.2021.
4. Hillaireau, H., Couvreur, P. (2009) *Cell. Mol. Life Sci.*, 66, 2873–2896.
5. Karg, M., Pastoriza-Santos, I., Liz-Marzán, L., Hellweg, T. (2006) *ChemPhysChem*, 7, 2298–2301
6. Schmidt, S., Tavernaro, I., Cavelius, C., Weber, E., Kümper, A., Schmitz, C., Fleddermann, J., Kraegeloh, A. (2017) *Nanoscale Res. Lett.*, 12, 545.
7. Shi, Y., Hélary, C., Haye, B., Coradin, T. (2018), *Langmuir*, 34, 406−415.

Stimuli-Responsive Polymer-Coated Gold Nanourchins for Controlled Delivery of Dasatinib Hydrophobic Tyrosine Kinase Inhibitor

A-S. Tatar[1], M. Baia[2], S. Astilean[1], S. Boca[1,*]

[1] Nanobiophotonics and Laser Microspectroscopy Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babes-Bolyai University, Cluj-Napoca, Romania.
[2] Biomolecular Physics Department, Faculty of Physics, Babeș-Bolyai University, Cluj-Napoca, Cluj, Romania

Abstract:
Smart, or stimuli-responsive nanoparticles are an emerging sub-type of nanomaterials with outstanding promise for use in biomedical applications, as they can allow the release of the functional cargo at the cellular or subcellular target site, which is recognized *via* the use of molecular targeting moieties such as antibodies. Stimuli-responsive polymers can be used to coat plasmonic nanoparticles and offer them additional advantages beyond those related to the noble metal core, and, based on their particular physico-chemical properties, can even prompt convenient features such as loading of hydrophobic payloads.

Here, we present our results regarding the development of stimuli-responsive polymer-coated gold nanourchins (GNU) for the controlled delivery of a hydrophobic anti-leukemia drug, Dasatinib. The nanourchin shape has a more substantial surface-to-volume ratio compared to isotropic particles and thus more surface area to adsorb cargo molecules. The use of the amphiphilic stimuli-reactive polymer poly-[2(di-methyl-amino)ethyl meth-acrylate] (PDMAEMA) allows good loading of the hydrophobic drug, offers good hydro-solubility of the particles in aqueous medium, and ensures drug release in the acidic pH of the lysosomal conditions. We show our assessment of stimuli-triggered controlled assays in conditions mimicking the lysosomal microenvironment by spectroscopic methods such as UV-Vis-NIR extinction spectroscopy and Dynamic Light Scattering (DLS). Density Functional Theory (DFT) calculations were performed to understand the binding mechanism, affinity and conformation of Dasatinib molecules onto nanoparticle surface.

The nanocarriers show good stability and pH-triggered drug release in simulated lysosomal conditions which make them potential candidates as promising nanoplatforms for the delivery and release of hydrophobic drugs, with less side effects, lower drug doses, and diminished overall costs.

Acknowledgement: This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-PD-2019-0387, within PNCDI III.

Keywords: gold nanourchins, controlled release, tyrosine kinase inhibitor, DFT, Philadelphia$^{(+)}$ leukemia.

References:

1. M. Mackiewicz, J. Romanski, K. Drabczyk, E. Waleka, Z. Stojek, and M. Karbarz, (2019) Degradable, thermo-, pH- and redox-sensitive hydrogel microcapsules for burst and sustained release of drugs, *Int. J. Pharm.*, 569, 118589;
2. G. Guan, M. Wu, and M. Han, (2020) Stimuli-Responsive Hybridized Nanostructures, *Adv. Funct. Mater.*, 30, 1903439;
3. Tatar, A.-S., Jurj, A., Tomuleasa, C., Florea, A., Berindan-Neagoe, I., Cialla-May, D., Popp, J., Astilean, S., and Boca, S. (2019). CD19-targeted, Raman tagged gold nanourchins as theranostic agents against acute lymphoblastic leukemia. *Colloids Surf. B Biointerfaces* 184.

Gelidium corneum mediated synthesis of gold nanoparticles with enhanced antiinflamatory and antioxidant potential

N. González-Ballesteros [1,*], L. Diego-González [2,3], M. Lastra-Valdor [4], M. Grimaldi[5], A. Cavazza[5], F. Bigi[5,6], R. Simón-Vázquez [2,3], M. C. Rodríguez-Argüelles [1]

[1] CINBIO, Universidade de Vigo, Departamento de Química Inorgánica, 36310 Vigo, Spain.
[2] CINBIO, Universidade de Vigo, Grupo de Inmunología, 36310 Vigo, Spain.
[3] Instituto de Investigación Sanitaria Galicia Sur (IISGS). SERGAS-UVIGO.
[4] Centro de Investigación Marina, Universidade de Vigo, 36331 Vigo, Spain
[5] Dipartimento Scienze Chimiche, della Vita e della Sostenibilità Ambientale. Università di Parma, 43124 Parma, Italy.
[6] IMEM Parma-CNR, 43124 Parma, Italy

Abstract:

Among the different types of nanomaterials, gold nanoparticles (AuNPs) have attract considerable attention due to their physicochemical properties. Due to these properties, AuNPs are being studied for use in a large number of fields. For instance, in nanomedice they are being investigated both for the diagnosis and for the treatment of cancer [1]. Unfortunately, nowadays are still some limitations for their application in medicine. The traditional synthetic methods of synthesis employ toxic reagents and capping agents that limit their use in food industry and medicine. That’s one of the main reasons why researchers are moving to alternative methods for the synthesis of nanomaterials known as green or biological methods. In this kind of method the metals are reduced into nanoparticles employing natural products or organism [2]. In this regard, we propose the use of the red macroalgae *Gelidium corneum* for the preparation of an aqueous extract. which contain the bioactive compounds of the seaweed. This extract acts as the reducing and stabilizing agent for the production of gold nanoparticles (Au@GC). The active substances occurring in the extracts, and assessed by analytical techniques such as spectrophotometric assays and liquid chromatography, were polyphenols and carbohydrates. In this way, the bioactive components of the seaweed could improve the biocompatibility and the biological activity of the nanoparticles. Indeed, Au@GC showed a good cytocompatibility in two different cell lines (lung and liver) and preserved the antioxidant and anti-inflammatory properties of *Gelidium corneum*. Specifically, Au@GC reduced the release of reactive oxygen species (ROS) and inflammatory cytokines in cells exposed to an oxidant or an inflammatory stimulus.

In summary, the synthesis of AuNPs from a seaweed extract, such as *Gelidium corneum*, produces cytocompatible and more biologically active NPs, expanding their potential therapeutic application in inflammatory and oxidative stress-mediated diseases.

Keywords: Green synthesis, *Gelidium corneum*, AuNP, Biocompatibility, Immunotherapy, ROS.

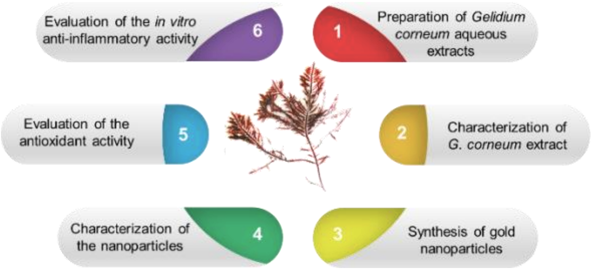


Figure 1: Schematic representation of the propose work plan for the revalorization of *G. corneum*

References:

1. Jindal, M., et al. (2020) Gold Nanoparticles-Boon in Cancer Theranostics, *Curr. Pharm. Des.*, 26, 5134-5151.
2. González-Ballesteros, N., Rodríguez-Argüelles, M. C. (2020), Seaweeds: A promising bionanofactory for ecofriendly synthesis of gold and silver nanoparticles, *Sustainable Seaweed Tecnologies Cultivation, Biorefinery, and Applications*, 507-541.

Enzyme-controlled Mesoporous Nanomachine for Triple-responsive Controlled Delivery

Beatriz Mayol[1]*, Victor Dato[1], Manuel Estravís[1], Cristina de la Torre[2,3,4], Paula Díez[2,3,4], Sandra Jimenez-Falcao[1], Anabel Villalonga[1], Félix Sancenón[2,3,4], Alfredo Sánchez[1], Paloma Martínez-Ruiz[1], Ramón Martínez-Máñez[2,3,4,5], and Reynaldo Villalonga[1]
[1] Department of Analytical Chemistry, Faculty of Chemistry, Complutense University of Madrid, Madrid, Spain
[2] Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Universitat Politècnica de València, Universitat de València, Valencia, Spain.
[3] Unidad Mixta UPV-CIPF de Investigación en Mecanismos de Enfermedades y Nanomedicina, Universitat Politècnica de València, Centro de Investigación Príncipe Felipe, Valencia, Spain.
[4] CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Spain.
[5] Unidad Mixta de Investigación en Nanomedicina y Sensores. Universitat Politècnica de València, Instituto de Investigación Sanitaria La Fe, Valencia, Spain.

Abstract:

During the last decades, progressive advances in nanotechnology are having a major impact on controlled release technologies for cancer therapy.[1] In this sense, a large variety of engineered nanomaterials have been proposed as innovative vehicles for antineoplastic drugs to allow their release at desired time and rate. Among the nanomaterials most employed for anticancer drug delivery, mesoporous silica nanoparticles (MSN) have attracted considerable attention due to their excellent structural, chemical and encapsulating properties, and their easy modification with stimuli-sensitive gate-like ensembles to yield "smart" nanocarriers for on-comand release.[2]

This work describes the construction of a MSN-based nanomachine with enzymatic control, able to release the payload in the presence of different stimuli: glucose, H_2O_2 and acid media. To this end, a novel and H_2O_2-sensitive 2-(benzo[d]thiazol-2-yl)phenyl 4-aminobenzoate derivative was synthetized and attached to MSN, previously loaded with the selected cargo. This nanomaterial was further functionalized with glucose oxidase modified with β-cyclodextrin moieties, to assemble a neglycoenzyme-based pH-sensitive supramolecular nanovalve.

This device released the encapsulated payload in the presence of H_2O_2 and acidic media. The use of glucose as input chemical signal also triggered cargo release through the enzymatic production of gluconic acid and hydrogen peroxide, and subsequent disruption of the gating mechanism at the mesoporous surface. The nanodevice was successfully employed for the enzyme-controlled release of doxorubicin in HeLa cancer cells in *in vitro* experiments.

Keywords: nanotechnology, nanomaterials, controlled delivery, mesoporous silica nanoparticles, enzyme, stimuli-responsive, nanomachine, doxorubicin, HeLa.

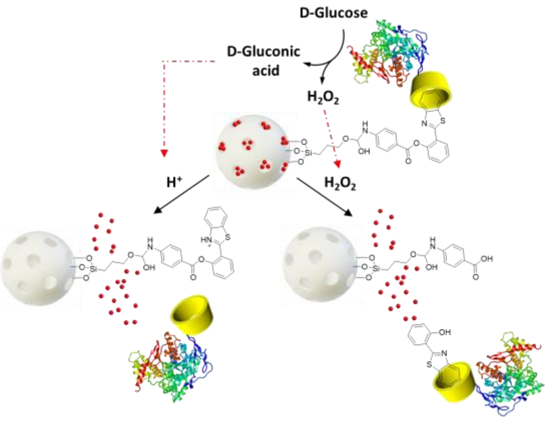


Figure 1: Schematic representation of the nanomachine architecture and performance.

References:

1. Klochkov, S. G., Neganova, M. E., Nikolenko, V. N., Chen, K., Somasundaram, S. G., Kirkland, C. E., & Aliev, G. (2021). Implications of nanotechnology for the treatment of cancer: Recent advances. *Semin. Cancer Biol.*, 69, 190-199.
2. Díez, P., Sánchez, A., Torre, C. d. l., Gamella, M., Martínez-Ruíz, P., Aznar, E., Villalonga, R. (2016). Neoglycoenzyme-gated mesoporous silica nanoparticles: Toward the design of nanodevices for pulsatile programmed sequential delivery. *ACS Appl. Mater. Interfaces*, 8(12), 7657-7665

Evaluation of green nanofibers-based composite materials as biosensor for selective glycoproteins detection

M. Florescu[1,*], M. David[1], K. Mamatkulov[2], G. Arzumanyan[2]
[1]Faculty of Medicine, Transilvania University of Brasov, Brasov, Romania
[2] Raman Spectroscopy Department, Frank Lab Neutron Physics, JINR, Russia
florescum@unitbv.ro

Abstract:
The use of green composite nanomaterials to enhance the study of biomolecular interactions is a promising route to develop new directions in medical applications. These nanomaterials are based on biologically synthesized metallic nanoparticles, specifically gold nanoparticles (AuNPs), and electrospun nanofibers. AuNPs obtained though plant synthesis show spectacular advantages given by their size and surface which can be tuned to possess various functionalities and good biocompatibility.

Here we describe the development of new composite nanomaterials, whose interaction with ligand molecules facilitates the binding of specific target molecules. By combining the green AuNPs with the nanofibers and phospholipids, new matrices of composite nanomaterials with improved characteristics were obtained. The characterization of these green nanofibers-based composite nanomaterials is very important for their further interaction with ligand biomolecules, when used in biosensors development for the selective detection of glycoproteins (Figure 1).

The characterization of composite nanomaterials was done using spectroscopic methods (UV-Vis absoption spectroscopy, electrochemical methods (CV, EIS), spontaneous and surface-enhanced Raman spectroscopy (SERS)) and atomic force microscopy (AFM). Characterization of the interactions between the composite nanomaterials and ligand biomolecules was done with by spontaneous Raman and SERS. The selective detection of glycoproteins using the developed green nanofibers-based biosensor was done using electrochemical methods and Raman/SERS spectroscopy.

Keywords: green gold nanoparticles, biological synthesis, electrospun nanofibers, composite nanomaterials, glycoproteins

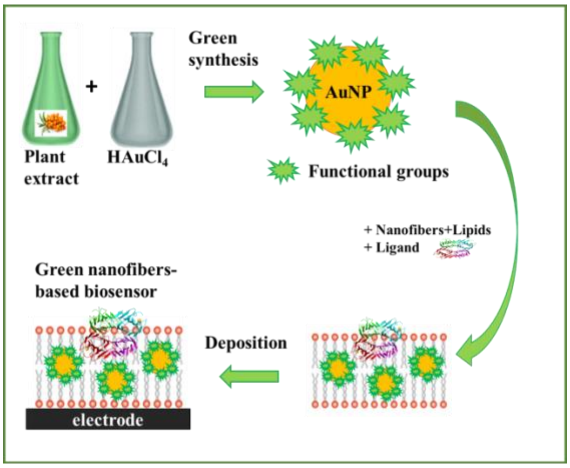


Figure 1: Figure illustrating the development of green composite nanomaterials-based biosensor for selective glycoproteins detection

Acknowledgments:
This work was supported by two projects: JINR-RO Joint Project, theme code 04-4-1133-2018/2023, Priority 1, theme name Modern Trends and Developments in Raman Microspectroscopy and Photoluminescence for Condensed Matter Studies and Ro-manian Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-PD-2019-1285, contract no. 123 within PNCDI III.

Determination of glucosamine hydrochloride used for the treatment of periodontal disease by high performance liquid chromatography

D. A. Scurtu [1*], O. Cadar [1], E. Kovacs [1], L. Senila [1], C. Roman [1]

[1] INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania

Abstract:
Nowadays, among the dental diseases, periodontitis affect the majority of the worldwide adult population. The symptoms are highlighted by the periodontal tissue inflammation and the loss of connective tissue and alveolar bone, which deteriorate the supporting bone of the teeth (jaw bone) leading to tooth loss.

Current clinical studies validate that the glucosamine use in the treatment plane of perodontis disease has a positive effect [1]. Glucosamine is a natural constituent of the human body, it is in especialy around joints, ligaments, tendons and cartilage. The commercial glucosamine can be obtained from the shellfish skeleton, less often is obtained using different laboratory procedures from the cereals fermentation process. The common used forms are glucosamine hydrochloride and glucosamine sulphate [2]. The higher purity of the hydrochloride glucosamine is 99% compared to 74% glucosamine sulphate which requires additional substance for stability.

High performance liquid chromatographic methods (HPLC) have been developed for determination of glucosamine in biological fluids and pharmaceutical samples [3]. Because the compound has no chromophore in its structure, a derivatization methods is requires. The with evaporative light scattering detector (ELSD) is able to detect all compounds that do not have chromophore groups [4].

A new method for determination of glucosamine hydrochloride by using high-performance liquid chromatography with evaporative light scattering detector (HPLC-ELSD) was developed. Method validation and uncertainty measurement were established.

Keywords: glucosamine hydrochloride, periodontal disease, high-performance liquid chromatography.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research CNCS-UEFISCDI, project number PN-III-P2-2.1-PED-2019-3664.

References:

1. Anyanechi C.E., Chukwuneke F.N., Ngim N. (2015), Clinical Evaluation of the Efficacy of Arthocare Forte, A Chondro-Protective and Anti-Arthritic Drug in the Management of Bacterial Plaque-Induced Chronic Periodontitis, *Ann. Med. Health Sci. Res.*, 5(3), 157-162.
2. Asthana C., Peterson G. M., Shastri M., Patel R. P. (2019), Development and Validation of a Novel High Performance Liquid Chromatography-Coupled with Corona Charged Aerosol Detector Method for Quantification of Glucosamine in Dietary Supplements, *PLoS One*, 14(5):e0216039.
3. Braun M., Ryglova S., Suchy T. (2021), Determination of glycosaminoglycans in biological matrices using a simple and sensitive reversed-phase HPLC method with fluorescent detection, *J. of Chromatography B*, 1173:122626.
4. Knol W. C., Pirok B. W. J., Peters R. A. H. (2021), Detection challenges in quantitative polymer analysis by liquid chromatography, *J. Sep. Sci.*, 44:63–87.

Biodistribution of Gold in Mice Tissues with Gold Nanostructured Compound Administration

O. Cadar [1*], M. Senila [1], A.I. Torok [1], T. Mocan [2,3]
[1] INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania
[2] Iuliu Hatieganu University of Medicine and Pharmacy, Physiology Department, Cluj-Napoca, Romania
[3] Regional Institute of Gastroenterology and Hepatology, Nanomedicine Department, Cluj-Napoca, Romania

Abstract:

Along with the increasing applications of nanomaterials in the medical fields, it is essential to know the systemic distribution of nanomaterials in the human body through a precise method for the biodistribution and biosafety assessment of nanomaterials. Gold nanoparticles have been widely used in biomedical sciences, *i.e.* drug delivery, therapeutics, imaging and diagnostics [1]. Therefore, precise, validated and easily applicable analytical tools are required to evaluate the biodistribution of gold in different tissue samples after gold nanoparticles administration [2].

This study aims to evaluate the biodistribution for a nanostructured, gold nanoparticle-based compound designed for immunoprophilaxy purposes. In this regard, we firstly set up a reliable, sensitive and reproductible analytical method based on the extraction by a new microwave-assisted digestion followed by graphite furnace atomic absorption spectrometry (GF-AAS) for concentration measurement of gold in biological tissues. Then, based on this method, the gold distribution in different mice was analyzed after gavage administration of gold nanoparticle-based compound. In vitro animal study carried out on house mouse (*Mus musculus*) and oral administration of gold nanoparticle-based compound was performed. Following single dose gavage administration of different amount of gold nanostructured compound in phosphate-buffered solution (PBS), the animals were sacrificed and the tissue samples (liver, small intestine, heart, lungs, brain and kidneys) were collected. Experimental protocol was carried out with the Institutional Committee approval. For the optimization of the microwave-assisted digestion procedure of biological tissue, different sample volumes, acidic mixtures and microwave programs were tested. The gold quantification was performed by GF-AAS and inductively coupled plasma mass spectrometry (ICP-MS) to evaluate the accuracy of the proposed method. After the optimization of the microwave-assisted decomposition procedure, this technology was used for the decomposition of mice tissues and the subsequent gold quantification.

Considering the obtained results, the proposed microwave-assisted decomposition platform demonstrates robustness, efficiency, and reliability. The proposed procedure demonstrated to be an outstanding method in the quantification of gold metallic nanoparticles-based compunds with complex matrices and a high content of organic matter, without the need of additional separation methods for the elimination of matrix interferences. Therefore, the developed microwave-assisted digestion procedure is an important tool for the gold quantification in biological tissues with metallic nanoparticles administration. Furthermore, these more comprehensive and important results would give fundamental information for the biological risk assessment of nanomaterials.

Keywords: gold nanoparticle, biodistribution,

microwave-assisted digestion, GF-AAS

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI –UEFISCDI, project number PN-III-P2-2.1-PED-2019-0844, within PNCDI III.

References:

1. Wu, M., Chen, L., Li, R., Dan, M., Liu, H., Wang, X., Wu, X., Liu, Y., Xu, L., Xie, L. (2018), Bio-distribution and bio-availability of silver and gold in rat tissues with silver/gold nanorod administration, *RSC Adv.*, 8, 12260.
2. Godoy, N.V., Galazzi, R.M., Chac´on-Madrid, K., Arruda, M.A.Z., Mazali, I.O. (2021), Evaluating the total gold concentration in metallic nanoparticles with a high content of organic matter through microwave-assisted decomposition platform and plasma-based spectrometric techniques (ICP-MS and ICP OES), *Talanta*, 224, 121808.

Determination of Trace Amounts of Silver in Various Simulated Biological Fluids by Graphite Furnace Atomic Absorption Spectrometry

O. Cadar [1*], D. Scurtu [1], A.M. Hoaghia [1], A. Ilea [2]
[1] INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania
[2] Iuliu Hațieganu University of Medicine and Pharmacy, Faculty of Dentistry, Cluj-Napoca, Romania

Abstract:
Silver (Ag^+) ions and silver nanoparticles (AgNPs) have a wide range of applications, mainly due to the well-known biological effect in different media of complex composition [1]. However, due to their potential toxicity for environmental and human health, analytical approaches for the determination of AgNPs in diverse and complex matrices for quality control and risk assessment are required. Understanding the complex behavior of NPs in biological fluids helps to check their biological effects and supports the design of their suitability for the desired goal. In this regard, the use of simulated biological fluids is an up-and-coming *in vitro* method to better understand the release mechanisms and possible *in vivo* behavior of various materials, such as fibers, metal nanoparticles and nanomaterials. Furthermore, the use of simulated biological fluids in dissolution tests allows the determination of material biopersistence or, contrarily, bioaccessibility (release mechanisms) that can offer a valuable inference of a materials biodistribution, as well as its acute, short- and long-term potential toxicity [2]. Nodaway, several analytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) can be used for the determination of Ag in various samples [3]. However, these methods suffer from severe matrix effects, especially at lower Ag concentration levels in biological and environmental samples. In this regard, an analytical method based on the microwave-assisted acid digestion of samples and atomic absorption spectrometry with graphite furnace (GF-AAS) was developed and validated for the determination of Ag from Ag-ZnO NPs [4] and $AgNO_3$ as a reference to account for Ag^+ ions released, after immersion in two simulated biological media, namely artificial human saliva and simulated body fluid. The selectivity study showed no significant matrix and spectral effects, while the linearity study was conducted for the calibration curve in the concentration range of 0-20 ng/mL. Also, the possible formation of AgCl due to the high concentrations of Cl^- ions in the simulated fluids was also evaluated. The amount of Ag^+ ions in both simulated solutions first increased and then decreased since Ag^+ ions reacted with Cl^- ions to form AgCl. The development and validation of a method for the determination of Ag in different simulated biological media provides a basis for future bioavailability and toxicological studies of Ag with potential application to other synthetic nanoparticles and/ or similar human biological matrices.

Keywords: silver, simulated biological fluids, GF-AAS, microwave digestion.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research CNCS-UEFISCDI, project number PN-III-P2-2.1-PED-2019-3664.

References:

1. Loza, K., Diendorf, J., Sengstock, C., Ruiz-Gonzalez, L., Gonzalez-Calbet, J.M., Regi, Koller, M., Epple, M. (2014), The dissolution and biological effects of silver nanoparticles in biological media, *J. Mater. Chem. B*, 2, 1634-1643.
2. Innes, E., Yiu, H.H.P., McLean P., Brown, W., Boyles, M. (2021), Simulated biological fluids - a systematic review of their biological relevance and use in relation to inhalation toxicology of particles and fibres, *Crit. Rev. Toxicol.*, 51, 217-248.
3. Poitras, E.P., Levine, M.A., Harrington J.M., Essader, A.S., Fennell, T.R., Snyder, R.W., Black, S.L., Sumner, S.S., Levine, K.E. (2015), Development of an analytical method for assessment of silver nanoparticle content in biological matrices by inductively-coupled plasma mass spectrometry, *Biol. Trace Elem. Res.*, 163, 184-192.
4. Cadar, O., Roman, C., Gagea, L., Cernica, I., Matei, A. (2007), Modern materials with

Development and validation of a spectrometric method for the evaluation of biodistribution of gold nanoparticles

A.I. Torok [1*], C. Tanaselia, T. Mocan [2,3], O. Cadar [1]
[1] INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania
[2] Iuliu Hatieganu University of Medicine and Pharmacy, Physiology Department, Cluj-Napoca, Romania
[3] Regional Institute of Gastroenterology and Hepatology, Nanomedicine Department, Cluj-Napoca, Romania

Abstract:
Nanotechnology is an attractive and challenging science focused on the materials at nanoscale level and their use in various applications. Gold nanoparticles (AuNPs) are very attractive and versatile nanoparticles since they have a unique chemical and optical properties that can be capitalized upon so that the nanoparticles act as drug carriers. The physico-chemical characteristics of AuNPs (*i.e.* particle size, shape, surface chemistry, routes of administration, exposure doses andtime, biodistribution and accumulation in organs) considerably influence the behavior of AuNPs in biological media, determine their interactions at the cellular levels and, subsequently, impact their toxic effects. Various instrumental techniques are used for the quantification of gold such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), neutron activation analysis (NAA), atomic absorption spectrophotometry (AAS) and graphite furnance atomic absorption spectrometry (GF-AAS).

The present study aims to validate a simple inductively coupled plasma mass spectrometry (ICP-MS) method for the determination of AuNPs. Metal nanoparticles are frequently used in medical applications as an excellent drug molecules, delivered for small or biomacromolecules such as DNA, RNA, proteins and glycolipids. The developed and validated method will be used for the evaluation of biodistribution of AuNPs designed for immunoprophilaxy purposes. *In vitro* animal study as carried out on *Mus musculus* mice, oral administration of nanostructured compound, was performed. Study groups (n=6) were constructured as to assure diferent concentration of exposure. Following single dose gavage administration, the animals were sacrificed and the collection of tissue samples was carried out. Fresh tissue samples were subject to immediate freezing procedure (-20°C), before analyzes. Experimental protocol was carried out with the Institutional Committee approval. In order to determine Au nanoparticles from the mice tissues, the biological matrix was digested using a four-step microwawe digestion method. The sample preparation as well the ICP-MS parameters were optimized to achieve high signal-noise ratio for Au isotope and a high accuracy for the quantification of the Au nanoparticules from biological matrixes. The ICP-MS spectrometry is a widely used technique in many diverse fields for element analysis. Several parameters were taken into consideration to validate the method for Au nanoparticle determination using ICP-MS technique: the method was evaluated according to the linearity, minimum detection limit, limit of quantification, repeatability, accuracy and uncertainty.

Keywords: ICP-MS, gold nanoparticles, validation, biodistribution.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI –UEFISCDI, project number PN-III-P2-2.1-PED-2019-0844, within PNCDI III.

References:

1. Li, W.; Cao, Z.; Liu, R.; Liu, L.; Li, H.; Li, X.; Chen, Y.; Lu, C.; Liu, Y., (2019), AuNPs as an important inorganic nanoparticle applied in drug carrier systems. Artificial Cells, *Nanomedicine, and Biotechnology,*. 47(1), 4222-4233.
2. Noireaux, J.; Grall, R.; Hullo, M.; Chevillard, S.; Oster, C.; Brun, E.; Sicard-Roselli, C.; Loeschner, K.; Fisicaro, P. (2019) Gold Nanoparticle Uptake in Tumor Cells: Quantification and Size Distribution by sp-ICPMS., *Separations,* 6, 3.

SiO$_2$-decorated Parylene C micropillars designed to probe cellular force

Z. Fohlerova[1,2*], I. Gablech[1], A. Otahal[2], P. Fecko[2]
[1]Central European Institute of Technology, Brno University of Technology, Purkynova 123, 612 00 Brno, Czech Republic
[2]Department of Microelectronics, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technicka 3058/10, 61600 Brno, Czech Republic

Abstract:
Living cells sense and respond to mechanical signals through specific mechanisms that generate traction force. The quantification of cell forces using micropillars can be limited by micropillar stiffness, technological aspects of the fabrication and microcontact printing of proteins. In this work, we show “top-down” fabrication of a highly ordered array of SiO$_2$/Parylene C micropillars standing on the Si substrate that can be used as a probe to quantify the force generated from living cells. We develop the array of micropillars with an aspect ratio of 6 and 3.5 and spring constant of 4.7 µN µm^{-1} and 28 µN µm^{-1}, respectively. The upper part of individual micropillars is coated with a 250 nm layer of thermally deposited SiO$_2$, and the results confirm protein binding on the micropillars via the SiO$_2$ interface and non-adhesiveness on the micropillars’ sidewalls. The results show an absence of cytotoxicity for micropillar-based substrates and a dependence on its stiffness. Stiffer micropillars enhance cell adhesion and proliferation rate, and a stronger cellular force of ~ 25µN was obtained. The significance of the cellular force transducer here is the elimination of the micro-contact printing of proteins, given that the SiO$_2$ thin film allows the covalent binding of proteins or peptides, or simply enables a charge or different wettability properties on top of micropillars via SiO$_2$ chemistry. This could help to researchers to skip the fabrication of a PDMS stamp and to prevent the differences in printing quality. The second contribution of this work is to prove that the fabrication of pillars from Parylene C as the highly rigid material with a Young’s modulus of ~4 GPa can, compared to PDMS polymer used for pillar fabrication, broaden the range of material stiffness to be probed by cells and enables to develop higher aspect ratio pillars. The third advantage is that our micropillars stand on Si wafer and thus any warping of underlying polymer membrane does not have to be considered as it has been reported for PDMS with lower aspect ratio.

Keywords: Cellular force; micropillars; parylene C; silicon dioxide.

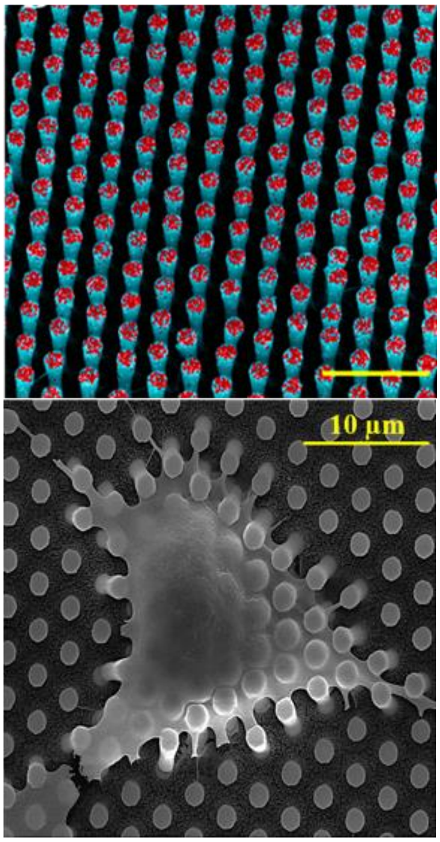


Figure 1: Figure illustrating the SiO$_2$ decorated parylene C micropillars. Oxide (red) is present just on the top of the pillars. The cells lying on of the micropillars with characteristic deflection of pillars from which the cellular foce is estimated.

References:

1. F. Viela, D. Granados, A. Ayuso-Sacido, I. Rodríguez, *Adv. Funct. Mater.* **2016**, *26*, 5599–5609.
2. W.J. Polacheck, C.S. Chen, *Nat. Methods* **2016**, 13, 415–423.

Selective Detection of Nickel Ions with Silver Nanoparticle-Based Sensor

Andrea Rossi[1], Marco Zannotti[1], Massimiliano Cuccioloni[2], Marco Minicucci[3], Laura Petetta[1], Mauro Angeletti[2], Rita Giovannetti[1]
[1]School of Science and Technology, Chemistry Division, University of Camerino, 62032 Camerino, Italy
[2]School of Biosciences and Veterinary Medicine, University of Camerino, 62032 Camerino, Italy
[3]School of Science and Technology, Physics Division, University of Camerino, 62032 Camerino, Italy

Abstract:

Silver nanoparticles (AgNPs) can be used as a surface plasmon resonance (SPR) colorimetric sensor; the correlation between the SPR phenomenon and the aggregation state of nanoparticle allows the real-time detection of a target molecule.

The color of nanoparticles is strightly related on their shape, dimension, composition, and dielectric constant [1], and it changes in the state of aggregation of nanoparticles. This dependence of SPAB on the state of aggregation is the principle for the detection of chemical substances by colorimetric sensors based on nanoparticles [2].

The functionalization of the nanoparticle surface is a common procedure used to increase/establish the sensor selectivity for a candidate analyte in a matrix containing other chemicals sharing similar properties [3]. Several classes of (bio)molecules can be used as NP functionalizing agents,

in particular, alkanethiols are often employed because of their ability to interact with the surface of the metal nanoparticles via their -SH tail [4].

This study reports on the synthesis of AgNPs under reducing conditions and on the functionalization thereof with mercaptoundecanoic acid (11-MUA). The prepared AgNPs@11MUA, eliciting a surface plasmon absorption band (SPAB) at 393 nm that shifted to 417 nm upon surface coating that is also investigated by Dynamic light scattering. Pelleted AgNPs@11MUA nanoparticles were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analyzers (EDX), and IR spectroscopy.

AgNPs@11MUA selectively detected micromolar levels of Ni^{2+}, also in the presence of other cations. These NPs were shown to associate into larger clusters in the presence of divalent cations that act as bridges between COO^{-} groups of 11MUA, eventually forming a "superlattice".

This aggregation phenomenon led to a major change in optical properties of the NPs suspension, with the progressive decrease in the intensity of the main SPAB at 417 nm and the appearance of a secondary SPAB at 477 nm, which increased in intensity with metal ions concentration. The higher rate in NPs clustering upon the addition of Ni^{2+} with respect to the other metal ions allowed the use of AgNPs@11MUA as a rapid colorimetric sensor for the qualitative detection of micromolar levels of Ni^{2+} ions in water with acceptable selectivity.

Keywords: colorimetric sensor; Ag nanoparticles; self-assembly functionalization; 11-Mercaptoundecanoic acid; Ni detection.

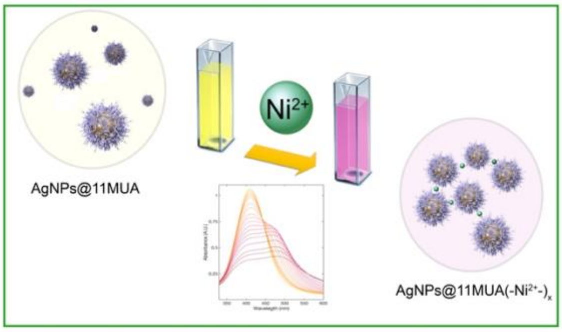


Figure 1: Schematic clustering process in the in the interaction of Ni^{2+} with AgNPs@11MUA

References:

1. Vilela, D.; González, M.C.; Escarpa, A. Sensing colorimetric approaches based on gold and silver nanoparticles aggregation: Chemical creativity behind the assay. A review. *Anal. Chim. Acta* **2012**, *751*, 24–43, doi:10.1016/j.aca.2012.08.043.
2. Sung, H.K.; Oh, S.Y.; Park, C.; Kim, Y. Colorimetric Detection of Co^{2+} Ion Using Silver Nanoparticles with Spherical, Plate, and Rod Shapes. *Langmuir* **2013**, *29*, 8978–8982, doi:10.1021/la401408f.
3. Pinelli, F.; Perale, G.; Rossi, F. Coating and Functionalization Strategies for Nanogels and Nanoparticles for Selective Drug Delivery. *Gels* **2020**, *6*, 6, doi:10.3390/gels6010006.
4. Pallavicini, P.; Dacarro, G.; Taglietti, A. Self-Assembled Monolayers of Silver Nanoparticles: From Intrinsic to Switchable Inorganic Antibacterial Surfaces. *Eur. J. Inorg. Chem.* **2018**, *2018*, 4846–4855, doi:10.1002/ejic.201800709.

Functionalized self-assembled AuNPs at the liquid-liquid interface with alkyne-based ferrocenyl derivative

Catalán-Toledo, J.[1], Crivillers, N.[1]
[1]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain
jcatalan@icmab.es

Abstract:

Interfacial self-assembling and functionalization of diverse nanoparticles have been intensively studied during the last decades. The organization of colloidal materials at the liquid-liquid interface promises an easy, low-cost alternative for the design and generation of large-scale chemically tuned nanoparticles arrays for diverse applications[1,2]. In this study, we present the interfacial self-assembly of aqueous ~5nm poly(vinylpyrrolidone) gold nanoparticles (AuPVP NPs) at the chloroform/water interface with the addition of a set of different alkynes (Dodecyne, Phenylacetylene, and Fc Stilb) in the organic phase, for the evaluation of carbon-gold (Au-C) bond formation and nanoparticles functionalization. The presence of different alkynes (aliphatic and/or aromatic) allows us to modulate the optical properties of the obtained nanoparticles films before the deposition on rigid substrates. In addition, electrochemical and vibrational spectroscopy studies allow us to confirm the chemisorption and C-Au formation of the alkyne-based ferrocenyl derivative and the effective anchoring at the nanoparticle surface, presenting the liquid-liquid interface as a suitable platform for nanomaterials functionalization with electroactive molecules. Finally, these films are potential candidates for the development of Surface Enhanced Raman Spectroscopy (SERS) platforms due to their architecture, organization, and response when they are deposited. In summary, here we present an economic, fast, and easy methodology for the development of self-standing films with the use of different alkyne ligands for the development of large-scale platforms for catalytic, electronic, and sensing applications.

Keywords: Gold nanoparticles, liquid-liquid interface, alkynes, surface functionalization, ferrocene derivatives, plasmonic tuning, surface-enhanced Raman spectroscopy.

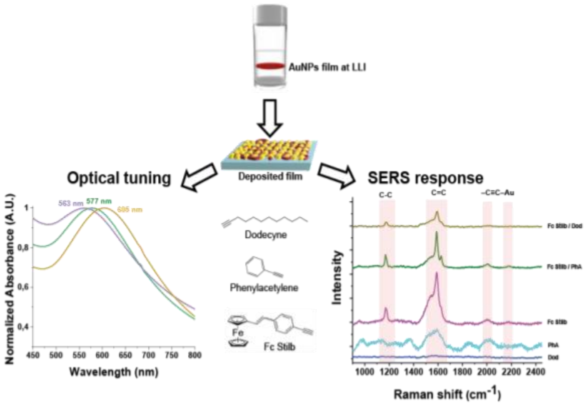


Figure 1: Schematic representation of the synthesis, deposition, and characterization of self-assembled AuNPs films at the liquid-liquid interface showing optical tuning and SERS response.

References:

1. Velleman, L., Sikdar, D., Turek, V. A., Kucernak, A. R., Roser, S. J., Kornyshev, A. A., & Edel, J. B. (2016). Tuneable 2D self-assembly of plasmonic nanoparticles at liquid| liquid interfaces. *Nanoscale*, *8*(46), 19229-19241.
2. Zarbin, A. J. (2021). Liquid–liquid interfaces: a unique and advantageous environment to prepare and process thin films of complex materials.*Materials Horizons*,*8*(5), 1409-1432.

Ferrocene-containing Porous Poly(ionic liquid) Membrane and its Conversion into Porous Iron Oxide Film

A. Khorsand Kheirabad [1], J. Yuan [1,*]
[1] Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

Abstract:
Poly(ionic liquid)s (PILs) are a unique subclass of polyelectrolytes, which were built up by polymerization of ionic liquids as monomers. The combination of anions and cations in ionic liquids with the macromolecular structure of polymers broadens the properties of polyelectrolytes and restructure the research profile of conventional polyelectrolytes. Currently more approaches are developing to produce porous membrane materials from PILs with various pore sizes and size distributions in different technologies, such as separation, filtration, catalysis and energy applications. Previously, our group has discovered a method to fabricate free-standing hierarchical (nano)porous PIL-based membranes using interpolyelectrolyte complexation process between a hydrophobic PIL and an organic week polyacid. Based on this procedure, an ionic crosslinking and a phase separation processes together can produce a 3D porous network and gradient of ionic crosslinking along the membrane cross-section due to the diffusion of aqueous ammonia into a casted PIL/polyacid blend film.
Herein, we will update you with our latest progress within the fabrication of porous polyelectrolyte membranes (PPMs) from an imidazolium-based PIL and a dicarboxylic acid compound containing the ferrocenyl unit. Further pyrolysis-treatment could transfer the iron-containing PPMs into porous iron oxide films. This process diversifies the application spectrum of PPMs and enables their function as sacrificial templates for the fabrication of inorganic porous films.

Keywords: poly(ionic liquid), ferrocene, porous polyelectrolyte membrane, iron oxide membrane

References:

1. Qian, W., Texter, J. Yan, F. (2017). Frontiers in poly (ionic liquid) s: syntheses and applications. Chem. Soc. Rev., 46, 1124-1159.
2. Lin, H., Zhang, S., Sun, J. K., Antonietti, M., Yuan, J. (2020). Poly (ionic liquid) s with engineered nanopores for energy and environmental applications. *Polymer*, 202, 122640.
3. Zhao, Q., Yin, M., Zhang, A. P., Prescher, S., Antonietti, M., Yuan, J. (2013). Hierarchically structured nanoporous poly (ionic liquid) membranes: Facile preparation and application in fiber-optic pH sensing. *J. Am. Chem. Soc.*, 135, 5549-5552.
4. Zhao, Q., Dunlop, J. W., Qiu, X., Huang, F., Zhang, Z., Heyda, J., Dzubiella, J., Antonietti M., Yuan, J. (2014). An instant multi-responsive porous polymer actuator driven by solvent molecule sorption. *Nat. commun.*, *5*, 1-8.

Porous Silicon-Based Microarray Platforms with Carbon Dots Functionalization for Enhanced Viral Detection

L. Gogianu[1], M.A. Popescu[1], A. Radoi[1], A. Sălceanu[1], A. Boldeiu[1], G. Craciun[1], M. Simion[1]

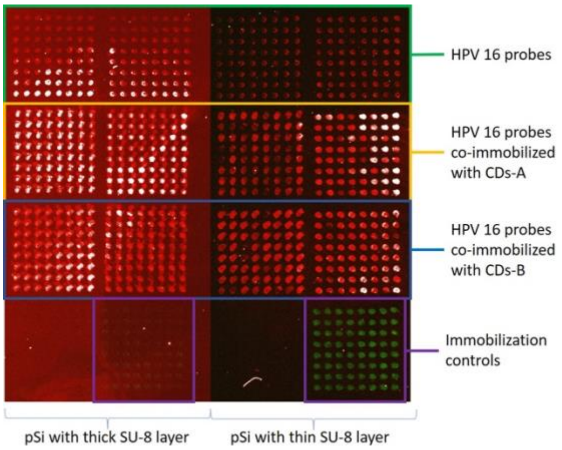
[1] National Institute for Research and Development in Microtechnologies – IMT Bucharest, 126A Erou Iancu Nicolae Street, 077190, Bucharest, Romania, email: larisa.gogianu@imt.ro

Abstract:

The three-dimensional (3D) configuration of microarray substrates gives better performance than the traditional glass and silicon-based surfaces in terms of higher probe binding capacity and improved hybridization yield [1,2]. The unique morphological, electrical, optical, and mechanical properties of carbon based nanomaterials recommend them for biomedical applications [3,4]. Here, we explored how the localized addition of carbon dots (CDs) on porous silicon (pSi) can potentially enhance the fluorescent signal of the DNA hybridization response in microarrays.

The porous silicon substrate improves the attachment of single-stranded (ssDNA) probes and increases the hybridization yield. Going further, the enhancement of the fluorescent signal is owed to the carbon dots co-immobilized with the ssDNA probes. **Figure 1** presents the hybridization results with HPV 16 amplicon obtained by assymetric PCR. The results are shown for pSi coated with two different SU-8 layer thicknesses.

Keywords: porous silicon, carbon dots, microarray, Human Papilloma Virus, DNA hybridization.


HPV 16 probes

HPV 16 probes co-immobilized with CDs-A

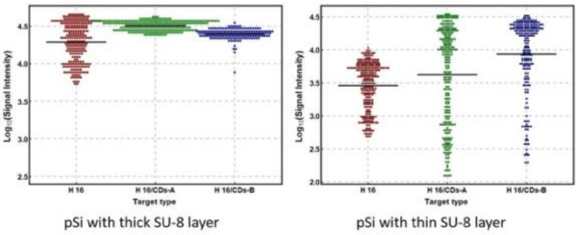
HPV 16 probes co-immobilized with CDs-B

Immobilization controls

pSi with thick SU-8 layer

pSi with thin SU-8 layer

Figure 1: Figure illustrating the hybridization results with HPV 16 amplicons obtained by assymetric PCR. The results are obtained on pSi coated with two SU-8 layer thicknesses. The microarray was achieved using the same laser power.



pSi with thick SU-8 layer

pSi with thin SU-8 layer

Figure 2 shows the graphical analyses corresponding to the HPV 16 hybridized with the a) ssDNA probes, b) ssDNA probes co-immobilized with CDs-A and c) ssDNA probes co-immobilized with CDs-B.

References:

1. RSC Adv Bouchloukh, W., Jouenne, B. (2012) Characterization of biofilms formation in urinary catheters, *Amer. J. Infect. Control.*, In Press.
2. Talanta Montoneri, F., Montoneri, E., Boffa, V., Sharts, O. (2011), Protein helical structure enhancement in fluorinated-phosphonate nanoporous silica glasses characterized by circular dichroism spectroscopy, *Int. J. Nanotech*., 8, 471-491.
3. Liu, J., Li, R., Yang, B. (2020), Carbon Dots: A New Type of Carbon-Based Nanomaterial with Wide Applications, *ACS Cent. Sci.* 6, 2179–2195.
4. Mihalache, I. et al. (2015), Charge and energy transfer interplay in hybrid sensitized solar cells mediated by graphene quantum dots, *Electrochim. Acta*, 153, 306–315.

Recent Progress of Nanoscale Metal-Organic Frameworks in Cancer Theranostics and the Challenges of Their Clinical Application

Bassem Sulaiman Salah Jadalh

Assiut University, Egypt

Abstract

The growing incidence of cancer raises an urgent need to develop effective diagnostic and therapeutic strategies. With the rapid development of nanomedicine, nanoscale metal-organic frameworks (NMOFs) presented promising potential in various biomedical applications in the last 2 decades, especially in cancer theranostics. Due to the unique features of NMOFs, including structural diversities, enormous porosity, multifunctionality and biocompatibility, they have been widely used to deliver imaging contrast agents and therapeutic drugs. Moreover, multiple types of contrast agents, anti-cancer drugs and targeting ligands could be co-delivered through one single NMOF to enable combination therapy. Co-delivering system using NMOFs helped to avoid multidrug resistance, to reduce adverse effects, to achieve imaging-guided precise therapy and to enhance anti-cancer efficacy. This review summarized the recent research advances on the application of NMOFs in biomedical imaging and cancer treatments in the last few years. The current challenges that impeding their translation to clinical practices and the perspectives for their future applications were also highlighted and discussed.

Keywords: nanomedicine, theranostic platform, biomedical imaging, combination therapy, clinical translation

THEVETIA PERUVIANA ROOTS EXTRACT MEDICATED GOLD NANOPARTICLES AND ITS UREASE INHIBITORY ACTIVITY

S. Bawazeer[1],
[1] Department Pharmacutical Chmistry, University Umm Al-Qura Univeristy, Makkah, Saudi Arabia

Abstract:

The main objective of the current research work was synthesized of gold nanoparticles (AuNPs) of *T. peruviana*’s aqueous extract, characterization and screening for urease enzyme inhibitory activity.

Gold nanoparticles (AuNPs) were synthesized by mixing 1 mM gold salt solution with *T. peruviana*’s aqueous extract without any reducing agents. The prepared AuNPs were characterized by using UV-visible spectroscopy, Fourier transform (FTIR) spectroscopy and scanning electron microscopy (SEM) techniques. The synthesized gold nanoparticles (AuNPs) were assessed for in vitro urease enzyme inhibitory activity at 0.2 µg in comparison with the aqueous extract.

In this finding we synthesized the gold nanoparticles (AuNPs) of *T. peruviana*’s aqueous extract for the first time. The AuNPs exhibited significant stability at room temperature. The AuNPs showed significant urease inhibitory activity with IC_{50} 67.56±1.67 at 0.2 µg as compared to aqueous extract which exhibited good activity with IC_{50} 39.21±1.32µ at 0.2 mg, against standard thiourea ($IC_{50=}$21.00 ±1.16). The formation of AuNPs correlates due to active phytochemical present in extract which are responsible for synthesizing nanoparticles.

In conclusion *T. Peruviana* extract and prepared AuNPs is an outstanding urease enzyme inhibitor and is capable of making fine nanoparticles. Application: The synthesized gold nanoparticles (AuNPs) of *T. peruviana*’s aqueous extract which significant urease inhibitory activity may allow us to discover nanoparticles for potentially effective and safe Nano herbal therapy.

Keywords: Thrvrtia peruviana,Extract, Nanoparticles, Urease activity

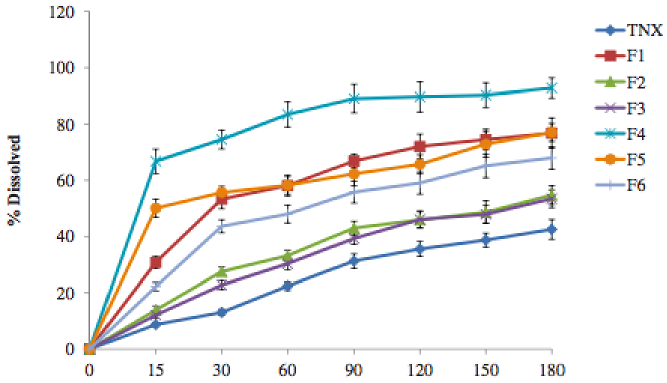


Figure 1: Different colors of graphs of gold nanoparticles show different ratios of gold salt versus plant .

References:

1. Samal K, Sahu HK, Gopalakrishnakone P. Clinico-pathological study of *Thevetia peruviana* (yellow oleander) poisoning. J Wilderness Med 1992;3:382-6.
2. Rao MA, Venkata E, Visweswaram D. Effect of certain structural changes in cardiac glycosides of *Thevetia peruviana* on their toxicity. J Mol Cell Cardiol 1978;10 Suppl 1:86-8.

Anthraquinone-carbon modified as hybrid electrode for energy storage system

S. Alshehri [1,2,*], G. Wildgoose [1], J. Fielden[1]

[a] School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, UK
[b] School of Chemistry, Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia

Abstract:

Electrografting of anthraquinone -2-diazonium chloride onto carbon electrode materials was successfully achieved using optimised cyclic voltammetry or chronoamperometric methods. A hybrid battery /supercapacitor has been constructed using anthraquinone as a cathode by electrografting of anthraquinone on the surface of carbon fibre electrode with lithium ions. Anthraquinone films have been studied by cyclic voltammetry, Galvanostatic (charge-discharge), impedance spectroscopy, and electrochemical quartz crystal microbalance (EQCM) and the effect of lithium with good electrochemical behaviour that shows specific capacitance (317 F/g) compare to anthraquinone-carbon fibre (AQ-CF) symmetric supercapacitor (158 F/g). Figure1 represents 40 cycles of anthraquinone film.

Keywords: Carbon fiber, Glassy carbon electrode,hybrid battery/supercapacitor, lithium ions.

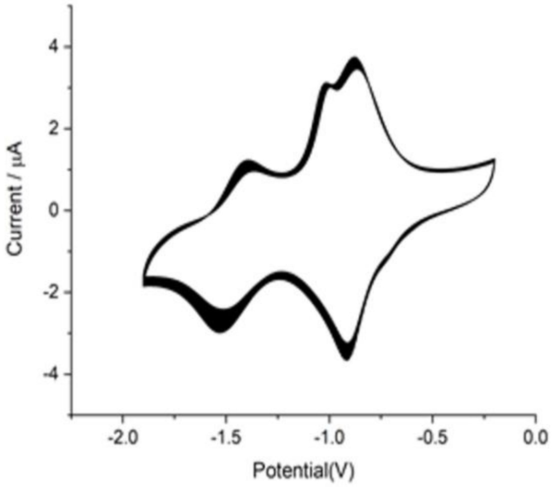


Figure 1:40 cycles of the redox waves of anthraquinone

Radiation Curable Hydrophobic Fluorinated Palm Oil based Urethane Acrylate Resin for Wood Coating Application

Nor Batrisya Ismail[1], Ain Najiyyah Jamaluddin[1], Norfazlinayati Othman[2], Mohd Sofian Alias[3], Khairul Azhar Abdul Halim[3], Mahathir Mohamed[3],
Rida Tajau[3] and Mohd Hamzah Harun[3*]

[1]Chemistry Department, Faculty of Science, Universiti Putra Malaysia,
43400, Serdang, Selangor, Malaysia
[2]Physics Department, Faculty of Science, Universiti Putra Malaysia,
43400, Serdang, Selangor, Malaysia
[3]Radiation Processing Technology Division, Malaysian Nuclear Agency, Bangi,
43000, Kajang, Selangor, Malaysia
Corresponding author: hamzah@nm.gov.my

Abstract

The aim of this study was to prepare hydrophobic coating from radiation curable palm oil resin for wood coating applications. Acrylated hydrophobic coating was prepared from palm oil based urethane acrylate (POBUA) by using the UV-curing technique. Five different sample formulations were prepared that used silica as the roughness agent, Perfluoroacrylate as the modifier and Irgacure-500 as the photoinitiator. Surface contact angle and IR spectroscopy were characterized for each sample. IR spectroscopy confirmed the presence of POBUA resins in all samples. Different formulations were prepared and the highest water contact angle value acquired is 116.3° which can be considered as a good hydrophobicity value for a wood coating application.

Keywords: radiation curable, hydrophobic coating, palm oil resin, wood coating

Bi-Layered Cantilever Based Opto-Mechanical Holographic Sensor

Faolan Radford McGovern[1,2,*], Catherine Grogan[1], George Amarandei[1], Izabela Naydenova[1,2*]

[1.] School of Physics and Clinical and Optometric Sciences, Technological University Dublin, Grangegorman, D07EWV4, Dublin, Ireland
[2.] Centre for Industrial and Engineering Optics, Technological University Dublin, FOCAS Research Institute, Camden Row, D08 CKP1 Dublin, Ireland.
[*]faolan.radfordmcgovern@tudublin.ie; izabela.naydenova@tudublin.ie

Abstract

The introduction of cantilever sensors which undergo a static deflection in the presence of a target analyte have allowed for enhanced sensitivity and stability in a panoply of scientific areas ranging from medicine to environmental sensing. Holographic sensors operation is based on detection of the variation of the optical properties of a diffractive element and have also garnered significant interest in a wide range of fields as they are low cost and highly adaptable. In this work a combination of the two aforementioned sensing technologies is presented resulting in a bi-layered cantilever sensor that encompasses two modes of sensing – a visual mode based on the static deflection of the cantilever and an optical mode based on the variation in the response of the diffractive optical element. The sensors working principle is based on a differential response of both layers to the target analyte – here the sensors methodology is demonstrated as effective in sensing changes to relative humidity. In this configuration the active photopolymer layer, in which the diffractive element is recorded, demonstrates hydrophilic properties while the inactive polydimethylsiloxane (PDMS) layer is hydrophobic. This leads to the active layer swelling/shrinking in response to changes in relative humidity and as a result a variation in the strain induced on the inactive layer. This leads to deflection of the cantilever which varies with the relative humidity in its environment. While relative humidity is used as an example of the effectiveness of this sensor configuration, this work also discusses methods through which the active photopolymer layer can be functionalised to allow for enhanced sensitivity to numerous target analytes while operating on the same sensing principles. Additionally, a comparison between the experimental results is conducted using COMSOL Multiphysics software. The modelling of a bi-layered cantilever is achieved using the COMSOL Structural Mechanics module utilizing the hygroscopic swelling node to simulate changes in relative humidity and model the cantilever response. The simulations demonstrate a similar trend to the experimental work, but an optimization is required to achieve a better agreement between the modelling and experimental results leading to a better understanding of the factors that determine the sensor sensitivity.

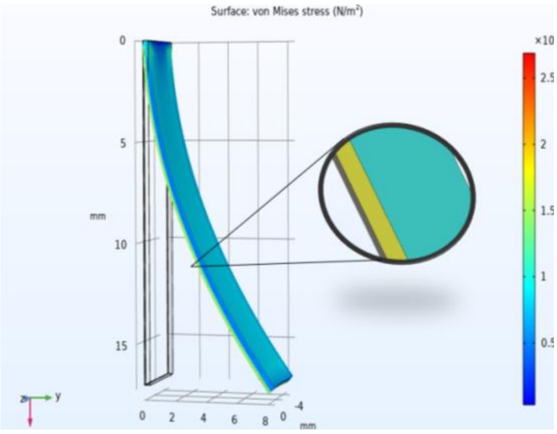


Figure 1: COMSOL Multiphysics Simulation of the Bi-Layered Cantilever Sensor

Development of volume holographic optical elements for application in wound healing monitoring

P. Stoeva[1,2], T. Mikulchyk [1,2], B. Rogers[1,2], M. Oubaha[3], S. Martin[1,2], D. Cody[1,2], M.A. Ferrara [4],
G. Coppola [4] and I. Naydenova [1,2.]
[1]Centre for Industrial and Engineering Optics/School of Physics and Clinical and Optometric Sciences, TU Dublin, Grangegorman, Ireland.
[2]The FOCAS Research Institute – TU Dublin, 13 Camden Row, Ireland, D08 CKP1.
[3]CREST, TU Dublin, 13 Camden Row, Ireland, D08 CKP1.
[4]ISASI-NA, 70, Via Pietro Castellino 111, 80131 Naples, Italy.

Abstract:

Chronic wounds demonstrate major healthcare challenges, where globally, the annual cost for wound care has been predicted to increase to 3.5 billion USD in 2021 [1]. They affect a broad population, exerting a severe financial burden and often resulting in amputation and grievous trauma. Benefits of sensing the wound environment include better understanding of conditions which impair the healing process, reduction of hospitalization time and expenses and overall, an improved patient experience. The ideal wound monitoring sensor should be reusable, cost-effective, and accessible. The development of such wound monitoring devices would also extend the reach of fundamental healthcare to secluded areas and even Space exploration. Holographic sensors have the potential to offer such benefits to healthcare systems worldwide due to their diverse sensing capabilities, physical properties (i.e., lightweight, flexible, and compact) and suitability for mass manufacturing [2]. Fundamental biochemical processes governing wound healing progression are related to elementary parameters, such as; oxygen, pH, temperature, and lactate. Real-time quantification of these parameters via holographic optical elements (HOEs) could allow for immediate estimation of the extent of local wound recovery. A speedy, patient-specific, and appropriate medical approach can then be suggested for treatment. Biocompatible water-resistant photosensitive materials suitable for specific functionalisation are utilised for the fabrication of wound monitoring sensors in this study.

The first part of this project focuses on the modelling and fabrication of a volume holographic waveguide capable of coupling a 633 nm LED light into a photopolymerised glass layer. The beam is redirected into the sensing site of a microfluidic chamber for oxygen monitoring based on photoluminescence. Transmission mode HOEs with a spatial frequency of 1697 lines/mm ± 5 lines/mm were recorded with a 532 nm beam as (a) slanted gratings (42°) and (b) lens (10 mm focal length) structures. Optimised layer preparation and recording conditions have resulted in the successful development of sol-gel coated couplers with a diffraction efficiency of up to 60 %. Significant environmental stability is revealed after UV bleaching of the photopolymerised glass layers. PDMS treatment with Dimethyl sulfoxide and UV has also shown improved layer adherence to sol-gel coatings demonstrating a promising future for HOE development on PDMS substrates.

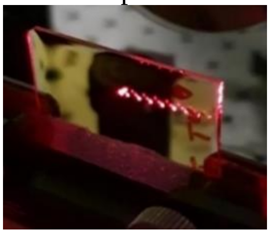


Figure 1: Slanted transmission mode sol-gel HOE waveguide probed at Bragg angle.

Acknowledgements

P.S. acknowledges the European Space Agency for supporting her MPhil scholarship. Thanks to Prof. Vincent Toal for many helpful discussions.

References:

[1] C. K. Sen, “Human Wounds and Its Burden: An Updated Compendium of Estimates,” Advances in Wound Care, vol. 8, no. 2, pp. 39-48, 2019.

[2] A. K. Yetisen, I. Naydenova, F. C. Vasconcellos, J. Blyth, C. R. Lowe, “Holographic sensors: three-dimensional analyte-sensitive nanostructures and their applications”, Chemical Reviews, vol. 114, no. 20, pp. 10654 - 96, 2014