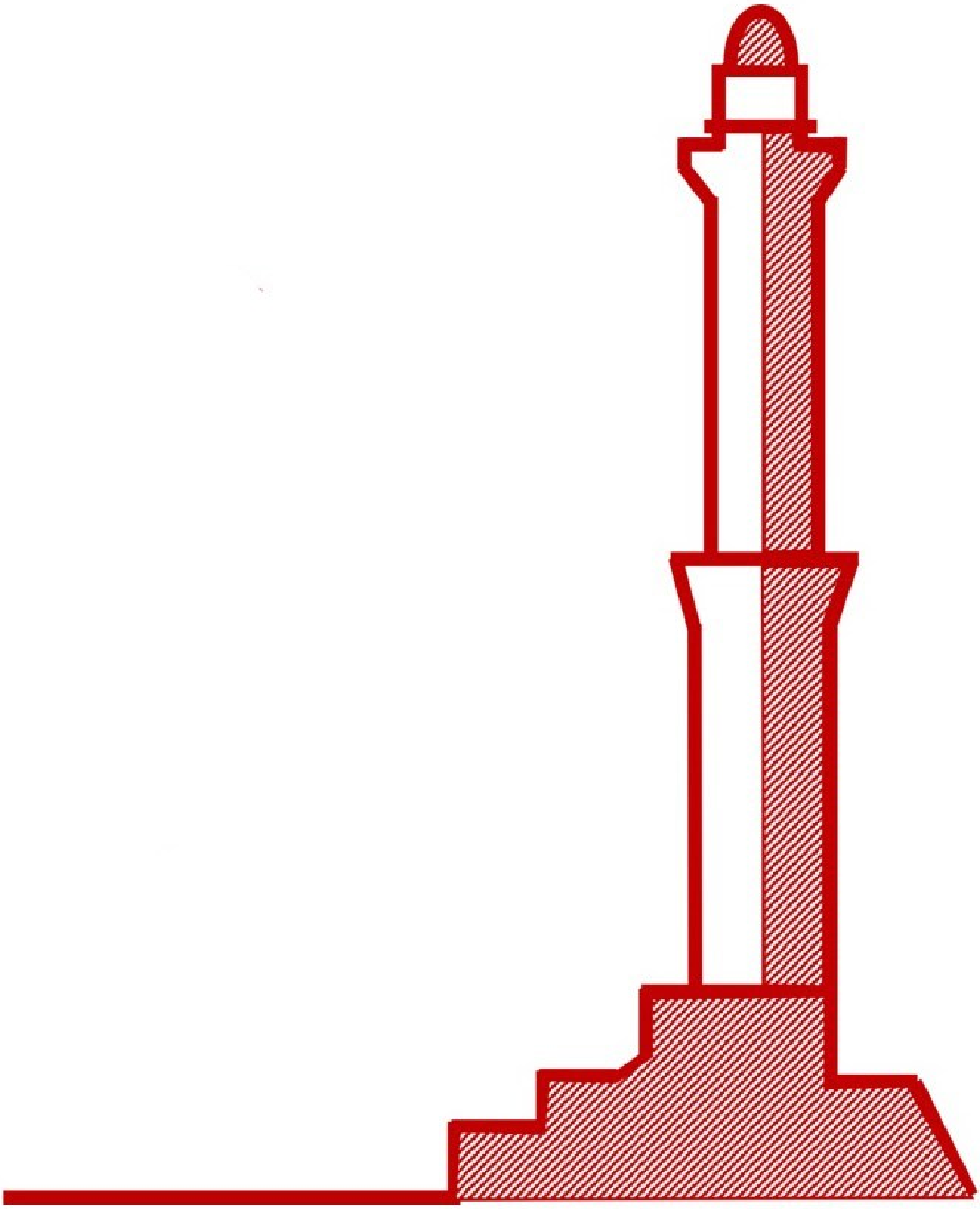
XLVIII CNCF

Genoa, 4-7 July 2022

XLVIII NATIONAL CONGRESS OF PHYSICAL CHEMISTRY

BOOK of ABSTRACTS



Atti del
XLVIII Congresso Nazionale

Genova, 4–7 luglio 2022

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Indice

Introduzione

Benvenuti al **XLVIII Congresso nazionale della Divisione di Chimica Fisica** della SCI!

Il XLVIII CNCF si e’ tenuto a Genova dal 4 al 7 luglio presso gli spazi del Dipartimento di Architettura e Design dell’Università degli Studi. L’evento costituisce come da tradizione un punto di incontro privilegiato per tutti coloro che in Italia, ma non solo, si occupano di chimica fisica in tutte le sue numerose declinazioni.

Ci rende particolarmente felici il fatto che il congresso rappresenti il ritorno in presenza dopo il tempo segnato dalla pandemia, a distanza di tre anni dall’edizione romana dell’evento. L’elevato numero di adesioni racconta del rinnovato desiderio di muoversi, di incontrarsi di persona e di confrontarsi sui propri risultati finalmente in modo diretto.

Questa XLVIII edizione porta un sottotitolo al passo con i tempi che stiamo vivendo, “La chimica fisica e le sfide della transizione ecologica”, e proprio nel segno di questo *slogan* diverse sono state le sessioni dedicate a temi ambientali e di conversione pulita dell’energia.

Ogni giorno i lavori sono stati aperti con una sessione plenaria tenuta da un illustre relatore, seguita da sessioni parallele. In totale abbiamo selezionato 213 contributi. Vari premi sono stati assegnati per evidenziare il merito degli speaker e l’alto livello delle loro presentazioni, riportati qui di seguito:

i. Medaglia Bonino: assegnata a socio della SCI, iscritto alla Divisione di Chimica Fisica, che si è distinto per i suoi contributi alla Chimica Fisica - *Giuseppe Zerbi*
ii. Giovanni Semerano Award: assegnato per la migliore tesi di dottorato in chimica fisica discussa l'ultimo anno - *Arianna Massaro e Arcangelo Celeste*
iii. Young Physical Chemist Award: assegnato alle migliori due comunicazioni orali, di iscritti alla Divisione di Chimica Fisica di età inferiore ai 35 anni alla data di inizio del Congresso - *Martina Fracchia, Tommaso Giovannini e Noemi Gallucci*
iv. Distinguished Physical Chemist Award: assegnato alle migliori due comunicazioni orali di iscritti alla Divisione di Chimica Fisica che si sono distinte per originalità e chiarezza
v. Lucio Senatore Award: assegnato al miglior poster - *Giorgia Mannucci*

Un ringraziamento speciale va dedicato agli sponsor del Congresso, che con il loro contributo e le stimolanti presentazioni, hanno riscosso un notevole interesse da parte del pubblico e permesso il dialogo con aziende di alto livello, confrontandosi sugli svariati temi della Chimica Fisica.

Inoltre, nel pomeriggio di mercoledì 6 luglio si e’ tenuta l’assemblea divisionale, seguita da una Tavola Rotonda aperta alla città. In questa occasione, c’e’ stato modo di discutere con esperti nel campo della transizione ecologica i punti chiave per invitarci, come scienziati, a lavorare con rinnovato entusiasmo e impegno per garantire uno sviluppo ecosostenibile e circolare dei progetti scientifici.

Vi ringraziamo per la partecipazione al XLVIII CNCF!

Plenary Lectures

Nanoscopy of Nanomaterials

Gustaaf Van Tendeloo, Sara Bals
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Electron microscopy has long been considered as a big magnifying glass. However in the 21st century it has evolved into a true analytical instrument able to provide information down to an atomic scale. This information not only relates to the atomic positions, but also to the chemical nature of the elements as well as the electronic state.

For micrometer or millimeter size materials without too many defects or secondary phases such information is obviously also available through other techniques (XRD, EXAFS, Raman, …), but for nanometer size materials or highly faulted materials most of these techniques fail.

Through scanning transmission electron microscopy (STEM) we can focus the electron beam down to a size below 0.1 nm and record information step by step. However, the most progress has been made by combining several of these2D images, taken under different angles, into a 3D image; this is the so called electron tomography. Since about a decennium this is possible down to atomic scale [1,2]. For example, we have been able to determine atom positions of metallic nanoparticles containing over 100 000 atoms down to a precision of a few picometer. In this way it is possible to quantify lattice relaxation at surfaces or interfaces.

The combination of 3D STEM imaging and EELS also allows one to image composition and charge of the individual atoms. A nice illustration is the possibility to visualize and quantify the reduction of Ce^{4+} into Ce^{3+} for CeO_2 nanoparticles [3]. It turns out that the presence of Ce^{3+} is much more prominent along the (111) planes than along the (100) planes in case of truncated octahedra.

All these experiments are performed inside the high vacuum of the electron microscope; however, real chemical processes (such as catalysis) take place under ambient conditions or under different gas flows…

Apart from the recent progress in the instrument there has also been major progresses in the design and possibilities of the sample holders for the electron microscope. It is now possible to obtain atomic resolution at elevated temperatures and even under an external gas flow of e.g. oxygen or hydrogen. These external gasses strongly influence the shape (and therefore the reactivity) of the metallic nanoparticles [4]. Evidently this is of uttermost importance for catalytic research.

[1] S. Van Aert et al. Nature 470 (2011) 374
[2] B. Goris et al. Nature Materials 11 (2012) 930
[3] B. Goris et al. ACS Nano 8 (2014) 10878
[4] T. Altantzis et al. Nano Letters 19 (2018) 477

PL001

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TALK TITLE

Nanoscopy of Nanomaterials

BIO-SKETCH

Gustaaf Van Tendeloo is a solid state chemist/physicist and materials scientist. He is a member of the EMAT research group (Electron Microscopy for Materials Science) of the University of Antwerp. His research is focusing on the characterization of inorganic and metallic (nano)materials, mainly through advanced electron microscopy. For his work he received an Advanced ERC grant (2010) and several awards, including the prestigious FWO Excellence Award (2015).
He is also a strategic scientist at the Technical University of Wuhan (China) and guest professor at Zhejiang University (China). His work has been cited over 60 000 times, resulting in an h-index over 100.

Macromolecular flexibility and the experimental determination of conformational landscapes by cryo Electron Microscopy

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We focus on analyzing macromolecular flexibility from cryo Electron Microscopy images without the constraint that images must come from a discrete set of conformations, which is a paradigm change in the way cryo EM data are currently handled in most cases. We do that by calculating the 3D deformation field and how every image contributes to it, obtaining information of the macromolecule conformational space. The deformation field we obtain is very rich, richer that what discrete conformations traditional cryoEM software can describe, and it can be explored in a variate of ways, leading to a better understanding of macromolecular motion. We present in Figure 1, up, an example of the type of conformational information provided by Zernikes3D, where the bases space is non-linearly projected onto a 2-dimensional plot where each point is an experimental image. This data cloud can now be explored systematically, extracting the experimental conformational variability present in the data

Also, and not with the goal of flexibility exploration but with the one of helping structural model tracing in difficult cases, we can partially “undo” the so obtained deformation field, increasing the resolution of “motion blurred” areas of the map. This is presented in Figure 1, from bottom left to right, where the improvement of map resolution between not applying any motion correction and applying it is evident. We have used our experimental data on SARS-Cov2 spike for the illustration.

Finally, we note that this experimental information on conformational landscapes can now be coupled to Molecular Dynamics analysis, trying to capture in this way a notion of time, eventually of “trajectory” and, also, higher resolution atomistic detail. It is currently one of the most powerful frameworks in which to integrate experimental information with computational capabilities.

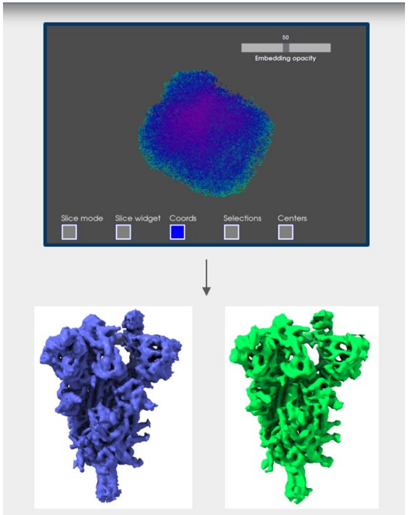

Figure Legend: Top: Zernikes3D-based two-dimensional representation of the conformational landscape of SARS-CoV2 spike in its 1-up position. Bottom: from left to right, the effect of explicitly considering conformational changes into the tree-dimensional reconstruction algorithm, helping model tracing.

PL002

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TALK TITLE

Cryo electron microscopy and the structure of macromolecules: new methods to study continuous conformational changes and the amazing possibilities they unlock

BIO-SKETCH

My field of work is cryo Electron Microscopy image processing, and I direct the BioComputing Unit (BCU) of the National Center for Biotechnology in Madrid. The BCU has always been an integrative environment where many synergies have emerged, including a successful startup that made all the way from conceptualization to acquisition by a US multinational in 2014. Currently I head several European projects (including one from the European Research Council, ERC), as well as National and Regional ones, with a substantial international impact (h-factor of 52 by Isi Web of Knowledge and of 67 by Google Scholar, with close to 10.000 citations). I direct the Spanish contribution to the European Research Infrastructure for Structural Biology, Instruct-ES, and I serve in several international and national Scientific Advisory Boards.

Boosting 2D materials with molecules for multifunctional opto-electronics and health monitoring

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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 to physisorb or chemisorb onto 2D materials in a controlled fashion, enabling functional diversification. [1]

In my lecture I will review our recent works on the functionalization of 2D materials to engineer hybrid systems via the controlled interfacing of the two surfaces of 2D semiconductors either in a symmetric or asymmetric fashion with molecular switches, to confer additional properties to WSe_2, thereby rendering 2D material-based transistors capable to respond to four different independent stimuli.[2]

The covalent functionalization of solution-processed semiconducting TMDs (MoS_2, WS_2 and ReS_2) was employed to simultaneously heal sulfur vacancies in metal disulfides and covalently bridge adjacent flakes, thereby promoting percolation pathways for charge transport, yielding a significant enhancement of the transistor characteristics.[3]

Finally, the controlled formation of multilayer structures of reduced graphene oxide and flexible molecular spacers made it possible to fabricate highly sensitive pressure and strain sensors for health monitoring [4].

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.

[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. (iii) Y. Zhao, M. Gobbi, L. Hueso, P. Samorì, Chem. Rev., 2022, 122, 50–131.
[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., Adv. Funct. Mater., 2021, 31, 2102721
[3] S. Ippolito, et al, Nat. Nanotech. 2021, 16, 592.
[4] C.-B. Huang, S. Witomska, A. Aliprandi, M.-A. Stoeckel, M. Bonini, A. Ciesielski, P. Samorì, Adv. Mater. 2019, 31, 1804600.

PL003

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Boosting 2D materials with molecules for multifunctional opto-electronics and health monitoring

BIO-SKETCH

Paolo Samorì is Distinguished Professor at the University of Strasbourg, Director of the Institut de Science et d'Ingénierie Supramoléculaires (ISIS). He is Foreign Member of the Royal Flemish Academy of Belgium for Science and the Arts, Fellow of the Royal Society of Chemistry, Member of the Academia Europaea, Fellow of the European Academy of Sciences, Member of the European Academy of Sciences and Arts and Senior Member of the Institut Universitaire de France. He obtained a Laurea in Industrial Chemistry at University of Bologna in 1995 and a PhD in Chemistry at the Humboldt University of Berlin in 2000. He was research scientist at Istituto per la Sintesi Organica e la Fotoreattività of the CNR of Bologna from 2001 to 2008 and Visiting Professor at ISIS from 2003 to 2008. He published 400+ papers on nanochemistry, supramolecular sciences and materials chemistry with a specific focus on 2D materials and functional organic/polymeric and hybrid nanomaterials for application in optoelectronics, energy and sensing. He was awarded numerous prestigious prizes. He is Associate Editor of Nanoscale (RSC) and Member of the Advisory Boards of 15 journals (ACS, Wiley, RSC, Nature Springer).

Applications of Infrared Multiple Photon Dissociation Spectroscopy to unravel the structure and reactivity of biomolecules in the gas phase

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Tandem mass spectrometry (MS/MS) is a key methodology to study biomolecules, with the electrospray ionisation (ESI) being one of the preferred ionization techniques [1]. It is well recognized as an efficient and highly versatile analytical tool [2], however its potential has long been limited by the structural information it can provide. For this reason, the combination of tandem mass spectrometry with IR Multiple Photon Dissociation (IRMPD) spectroscopy has become a powerful tool for 3D structural characterisation of molecular ions in the gas phase [3]. Exploiting highly intense and widely tunable Free Electron Laser (FEL), IRMPD spectroscopy allows for the derivation of the vibrational fingerprint of molecular ions under tandem mass spectrometry (MS/MS) conditions [4]. Because resonant absorption of IR photons depends on molecular vibrations, the subsequent fragmentation event is highly structure specific, revealing characteristic functional groups of the molecule.

In this contribution, several examples of IRMPD spectroscopy applied to the study of biomolecules or prebiotic molecules performed at CLIO facility in Orsay will be presented [5].

First of all, I will illustrate how IRMPD spectroscopy can provide insight into the nature and localization of posttranslational modifications (PTMs) affecting single amino acids and peptides [6,7]. A posttranslational modification (PTM) is a covalent modification occurring downstream after DNA has been transcribed into RNA and translated into proteins [8]. PTMs typically affect the side chain of amino acid residues. The impact of a PTM on a local protein conformation often spurs signalling initiation. Considerable effort is obviously devoted to develop strategies to evaluate such a rich and varied landscape and to contribute to build an integrated systems biology vision. In the second part of my talk, I will present a novel approach developed to synthesize molecules relevant to prebiotic chemistry, using Infra-Red (IR) radiation to trigger the reaction. Understanding how prebiotic molecules can be formed under the early-earth conditions by elementary reactions is at the center of many investigations and IR-induced molecule formation also deserves research since it is a low-energy and widely present radiation. This novel approach is applied to the possibility of forming glycine, the simplest amino-acid [9].

[1] C. M. Whitehouse et al. Anal. Chem. *57 (*1985) 675
[2] J.D.Bridgewater et al. J. Am. Soc. Mass Spectrom. (2007) 18 553
[3] A. Rijs and J.Oomens, In Topics in Current Chemistry, Vol. 364, Spring Edition, 2015
[4] J. Oomens et al. *ApJ* 542 (2000) 404 ; J. Lemaire et al. Phys. Rew. Lett. 89 (2002) 273002
[5] R. Prazeres et alt. Eur. Phys. J. D 1 (1998) 87
[6] P. Maitre et al. Chem. Rev. 120 (2020) 3261
[7] D.Scuderi et al. Chem. Eur. J. 22 (2016) 17239
[8] C.T. Walsh, Posttranslational Modifications of Proteins: Expanding Nature's Inventory, Roberts and Co.: Greenwood Village, CO, 2006
[9] D. Scuderi et at. Chem. Phys. Chem.21 (2020) 503

PL004

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TALK TITLE

Applications of Infrared Multiple Photon Dissociation Spectroscopy to unravel the structure and reactivity of biomolecules in the gas phase

BIO-SKETCH

Debora Scuderi is Assistant Professor of Physical Chemistry at Université Paris Saclay in Orsay (France). She received her Laurea degree in Chemistry in 2000 at the Sapienza Università di Roma, working in the Laboratory of Prof. Anna Giardini. In 2003, she earned her Ph.D. in Chemistry at this same university under the guidance of Prof. M. Speranza. During 2003-2005, she pursued a postdoctoral fellowship in the Laboratory of Applied Optics in Ecole Polytechnique (France).

She is actually scientific responsible of the Free Electron Laser Facility CLIO in Orsay and of the Orsay site of the network of Fourier Transform Resonance Mass Spectrometer (FT-ICR) InfraAnalytics.

She became in 2022 president of the French Chemical Physical Division. She has been several time visiting professor at “La Sapienza” University in Simonetta Fornarini’s group. Her current research, at the FEL CLIO in Orsay, focus on IR and UV spectroscopy of mass selected ions in the gas phase. She is mainly involved in studying and understanding energetic, structure and reactivity of modified biomolecules, by using mass spectrometry-based methods.

Photocatalytic production of Hydrogen from Hydrogen Sulfide: an experimental study and technoeconomic evaluation

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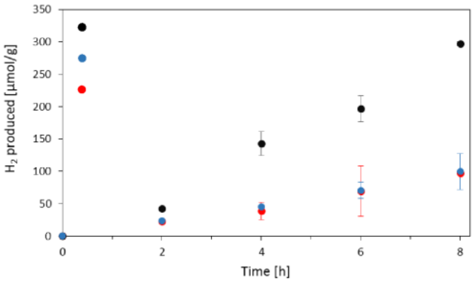
Hydrogen is widely considered a clean source of energy (HHV = 142 MJ kg) because its combustion by-product (water) is nontoxic and is environmentally benign compared to fossil-based fuels[1]. Hydrogen has long been produced from pyrolysis and reforming of fossil fuels, coal, biomass etc. Recent alternative routes like solar-assisted splitting of water have also received a lot of attention. Although water splitting exhibits a minor carbon footprint compared to fossil-fuels, it remains a thermodynamically difficult process (ΔG = 294.7 kJ mol^{-1}). This calls for exploration of less thermodynamically demanding feedstock such as H_2S (ΔG = 294.7 kJ mol^{-1})[2]. In the oil and gas industry, H_2S is considered a waste product – occurring naturally or as by-product of sour gas sweetening, hydrodesulfurization of hydrocarbons, and upgrading of heavy oil[3]. The abundance of H_2S in oil and gas processes poses environmental and economic challenges. While many technologies have been used to remove this gas waste from oil and gas streams, the photocatalytic H_2S splitting is not still fully explored. The aims of this work are to prepare novel Pt-decorated N-TiO_2/G with remarkable hydrogen generation from H_2S, study the mechanism of hydrogen production and perform techno-economic analysis of the photocatalytic H_2S splitting. Fig. 1 shows the hydrogen production over Pt/P25, Pt/N-P25 and Pt/N-TiO_2/G in 0.1 M Na_2S solution at its natural pH of 12.8. The corresponding concentrations of the ions in the reaction medium are 0.0586 M, 0.0414 M and 1.12 x 10^{-7} M for HS^-, S^{2-} and H_2S, respectively. The reaction order was observed to be zero-order kinetics and the production rate of hydrogen with Pt/N-TiO_2/G was twice that obtained over Pt/P25. For the economic analysis, at a NaOH price of 300 $/ton, a specific capital investment of 1.24 $/kg of H_2 and unit production cost of 1.7 $/kg of H_2 were estimated, and the profitable price of H_2 produced was estimated to be $1.82 /kg of H_2

[1] H. Oladipo, A. Yusuf, K. Al-Ali, and G. Palmisano, Energy Technology, 2021, 9, 2100163.
[2] H. Oladipo, C. Garlisi, J. Sa, E. Lewin, K. Al-Ali, and G. Palmisano, Applied Catalysis B: Environmental, 2020, 270, 118886.
[3] B. Cox, International Journal of Hydrogen Energy, 1998, 23, 531–544.



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TALK TITLE

Photocatalytic production of Hydrogen from Hydrogen Sulfide: an experimental study and technoeconomic evaluation

BIO-SKETCH

Giovanni Palmisano is an Associate Professor of Chemical Engineering at Khalifa University, where he leads activities in the field of photocatalysis and he teaches undergraduate and graduate courses. He has been the recipient of the 2015 and 2017 Abu Dhabi Department of Education and Knowledge (ADEK) Award for Research Excellence and the 2018 Faculty Research Excellence Award granted by Khalifa University for the category “Associate Professor” of the College of Engineering. His research activities are mainly focused on photocatalysis applied to water, environment, materials functionalization, energy, and organic chemistry and they are regularly funded by internal and external grants. He is the co-author of ca. 120 highly cited journal papers, eight patents, seven books and nine book chapters and one of the Associate Editors of the Journal of Environmental Chemical Engineering (Elsevier). He has been main advisor of six Ph.D. students and four M.Sc. students, one of whom won the outstanding thesis award in Masdar Institute.

Invited Oral Contributions

Computer Generated Realistic Interstellar Icy Grain Models: Physico-chemical Properties and interaction with NH_3

Piero Ugliengo[1], Aurele Germain[1], Lorenzo Tinacci[1,2], Stefano Pantaleone[1], Cecilia Ceccarelli[2]
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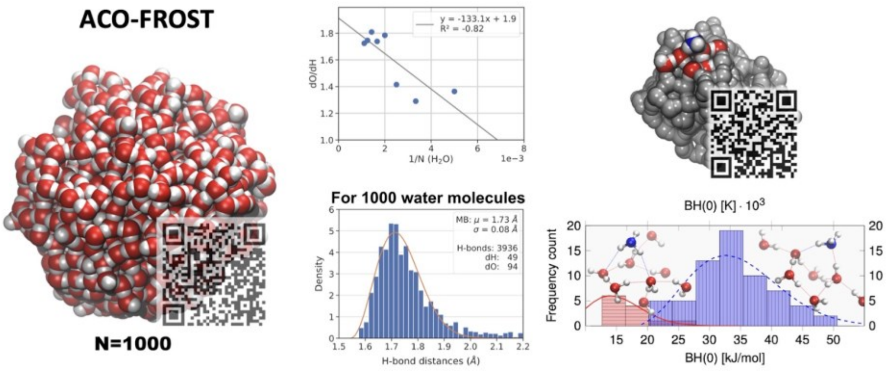
Interstellar grains are composed by a rocky core (usually amorphous silicates) covered by an icy mantle, the most abundant molecule being H_2O followed by CO, CO_2, NH_3 and also radicals in minor quantity [1]. In dense molecular clouds, gas-phase chemical species freeze onto the grain surface making it an important reservoir of molecular diversity/complexity whose evolution brings to interstellar complex organic molecules (iCOMs). Many different models of water clusters have appeared in the literature, but without a systematic study on the properties of the grain (such as the H-bonds features, the oxygen radial distribution function, the dangling species present on the mantle surface, the surface electrostatic potential, etc.). In this work, we present a computer procedure (ACO-FROST) grounded on the newly developed semi-empirical GFN2 tight-binding quantum mechanical method [2] and the GFN-FF force field method [3] to build-up structures of amorphous ice of large size. These methods show a very favorable accuracy/cost ratio as they are ideally designed to handle non-covalent interactions. The ACO-FROST program can be tuned to build grains of different composition, but also dirty icy grains. These icy grain models allow to study the adsorption features (structure, binding energy, vibrational frequencies, etc.) of relevant species on a large variety of adsorption sites to obtain a statistically meaningful distribution of the physico-chemical properties of interest to be transferred in astrochemical numerical models. In the present case, accurate quantum mechanical simulation of NH_3 adsorption will be described [4].



[1] A. Boogert, P. Gerakines, D. Whittet, Annu. Rev. Astron. Astrophys 53, 541-581 (2015).
[2] C. Bannwarth, S. Ehlert, S. Grimme, J. Chem. Theory Comput 15, 1652-1671 (2019).
[3] S. Spicher, S. Grimme, Angew. Chem 59, 15665-15673 (2020)
[4] A. Germain, L. Tinacci, S. Pantaleone, C. Ceccarelli, P. Ugliengo, ACS Earth & Space Chemistry, DOI: 10.1021/acsearthspacechem.2c00004

KN001

Nanoengineered Al-doped ZnO thin films for heat harvesting

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Nanoengineering approach has been applied on thin films of Al-doped ZnO (AZO) prepared by several techniques with the purpose of enhancing their thermoelectric performance.

At first, epitaxial thin films of AZO films were fabricated by pulsed laser deposition (PLD) on several single crystal ($SrTiO_3$, Al_2O_3) and amorphous (silica) substrates. Independently on the substrate, films always shows higher values of $ZT = \sigma S^2 \times T/\kappa$ (figure of merit: σ = electric conductivity, S = Seebeck coefficient; T = temperature and κ = thermal conductivity) in comparison with corresponding bulk AZO: for example at T = 600 K, $(ZT)_{AZO\text{-}on\text{-}STO} = 0.03$ [1,2]. The superior performance of films is due to their lower thermal conductivity: $\kappa_{AZO\text{-}on\text{-}STO}$ (300 K) = 6.5 W/m×K [1,2] while κ_{BULK} (300 K) = 34 W/m×K.

In this first series of films, the grain boundaries can be considered as natural nanodefects for enhanced scattering of phonons and consequent depression of κ respect to the bulk material. As demonstration of this effect, the film on fused silica, showing additional grain boundaries at the seed layer on the substrate, had even lower thermal conductivity: $\kappa_{silica\ (300\ K)}$ = 4.89 W/m×K.

Insertion of artificial nanodefects has been subsequently considered with the purpose of further depressing κ and enhancing ZT. Several approaches have been tried:

i. insertion of hydroquinone nanolayers in AZO films prepared by atomic layer deposition (ALD): $\kappa_{ALD\ (300\ K)}$ = 3.56 W/m×K [3];
ii. addition of polymetylmetacrilate (PMMA) particles to AZO films prepared by multi-beam multi-target matrix-assisted PLD (MBMT/MAPLE-PLD): κ_{MAPLE} (300 K) = 5.9 W/m×K [4];
iii. formation of nanopores in AZO films prepared by Mist-Chemical Vapor Deposition (Mist-CVD): κ_{porous} (300 K) = 0.60 W/m×K [5];
iv. dispersion of Al_2O_3 nanoparticulate in AZO films prepared by surface-modified target PLD: $\kappa_{nanoAl2O3}$ (300 K) = 3.98 W/m×K [6].

All these successful examples highlight the promise of nanostructured AZO films for future energy harvesting applications.

The author wants to acknowledge the International Research Center for Green Electronics (IRCGE), Shibaura Institute of Technology, for providing financial support.

[1] P. Mele, S. Saini, H. Honda et al., Appl. Phys. Lett. 102 253903 (2013).
[2] S. Saini, P. Mele, et al., Japan. J. Appl. Phys. 53 060306 (2014).
[3] T. Tynell, P. Mele, M. Karppinen et al., J. Mater. Chem. A 2, 12150 (2014).
[4] A.M. Darwish, A. Muhammad, S.S. Sarkisov, P. Mele et al., Composites B 167 406 (2019).
[5] S. Saini, P. Mele; T. Oyake; J. Shiomi et al., Thin Solid Films 685 180 (2019).
[6] P. Mele, S. Saini, T. Mori, Y. Kakefuda, M. I. Adam et al., in preparation

KN002

Physicochemical studies of i-motif-forming DNA sequences

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Under slightly acidic conditions, cytosine-rich DNA sequences can form non-canonical secondary structures called i-motifs, which occur as four stretches of cytosine repeats form hemi-protonated cytosine-cytosine ($C{\cdot}C^+$) base pairs (Figure 1) [1]. The growing interest in the i-motif structures as important components in functional DNA-based nanotechnology or as potential targets of anticancer drugs [2], increases the need for a deep understanding of the energetics of their structural transitions.

Here, a combination of spectroscopic and calorimetric techniques is used to unravel the thermodynamics of folding of an i-motif DNA under favorable conditions and to investigate the pH-dependent conformational equilibria of biologically relevant i-motif-forming sequences [3,4]. Our experimental results provide new insights into the energetic aspects of i-motifs, including the contribution of cytosine protonation, and show that thermodynamic and thermal stability are related but not identical properties of such DNA structures. Moreover, these studies shed some light on the factors that can influence at the molecular level the equilibrium between different conformational species of C-rich DNA sequences presumably involved in biological functions.

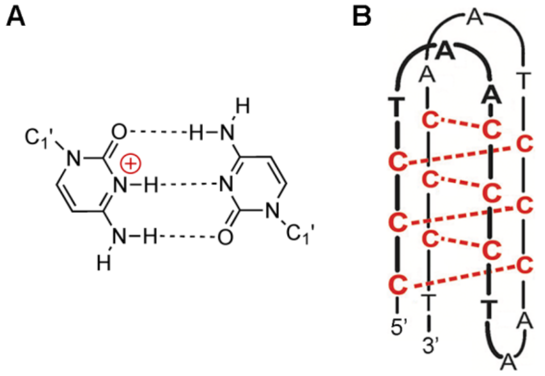

Figure 1. (A) Hemi-protonated $C{\cdot}C^+$ base pair. (B) Schematic representation of an i-motif structure.

[1] H. Abou Assi, M. Garavis, C. Gonzalez, M. J. Damha. Nucleic Acids Res. 46 (2018) 8038
[2] M. Debnath, K. Fatma, J. Dash. Angew. Chem. Int. Ed. 58 (2019) 2942
[3] J. Amato, F. D'Aria, S. Marzano, N. Iaccarino, A. Randazzo, C. Giancola, B. Pagano. Phys. Chem. Chem. Phys. 23 (2021) 15030
[4] J. Amato, N. Iaccarino, F. D'Aria, F. D'Amico, A. Randazzo, C. Giancola, A. Cesàro, S. Di Fonzo, B. Pagano. Phys. Chem. Chem. Phys. 24 (2022) 7028

KN003

Low-dimensional nanostructures at liquid interfaces: assembly and forces

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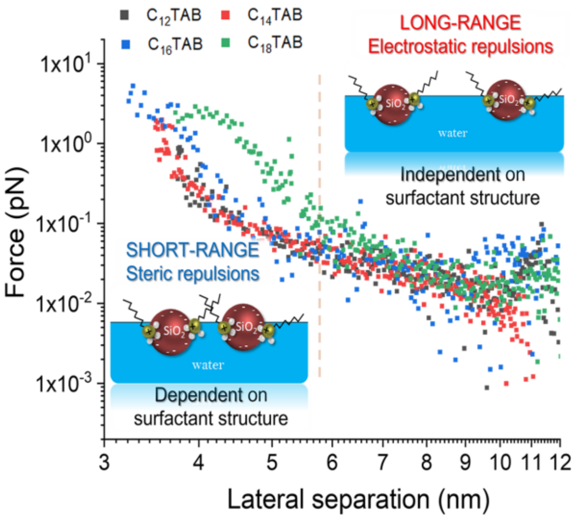
Last years have witnessed an increasing attention on the assembly of inorganic nanoparticles (NPs) at liquid interfaces, as it allows preparing nanostructured functional monolayers and low-dimensional systems. Among the various approaches, the spontaneous assembly of negatively charged NPs upon the addition of oppositely charged surfactants, proved to be an easy method to prepare homogeneous interfacial layers with controlled structure [1].
In this framework, we will show our most recent results demonstrating how it is possible to significantly enhance our ability to control the layer assembly and properties via precise formulation of the dispersion and, upon formation of the layer, via compression in a Langmuir trough. The significance of our results is twofold. On the one hand, they contribute to the development of liquid interfaces and low-dimensional systems with ultra-finely controlled nanostructure. On the other hand they provide new evidences helping to clarify the largely debated role played by the surfactant in the NP interfacial assembly [2,3]. Finally, it will be demonstrated how, by simultaneously compressing the monolayer and recording the inter-particle distance variation, it is possible to measure forces acting between NPs at the interface as a function of the inter-particle distance [4], thus providing a new tool to investigate the origin of the interfacial nanoscale forces and their propagation across two distinct media.



[1] L. Costa et al. Nano Lett. 16 (2016) 5463
[2] C. Li et al Adv. Mater. Interfaces 7 (2020) 2000391
[3] A. Maestro et al. Soft Matter. 8 (2012) 837
[4] G. Li Destri et al. Soft Matter 15 (2019) 8475

KN004

3D printing of magnesium-based cements: towards the preparation of bioceramics

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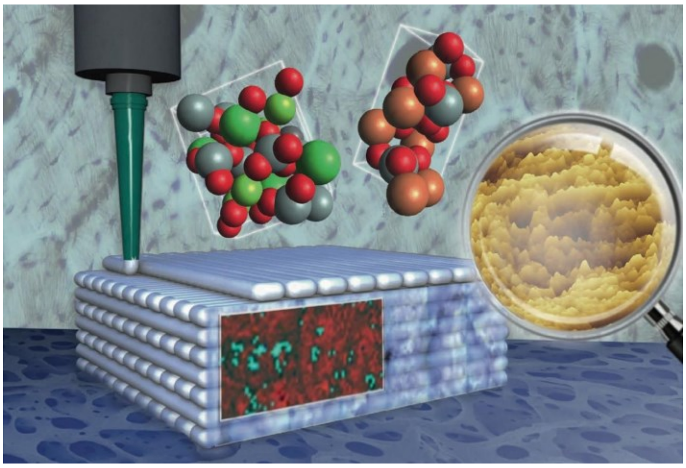
The recent progresses in additive manufacturing (AM) techniques and their exploitation in tissue engineering have imposed the need to develop new processable materials and, at the same time, to implement the properties of the materials already in use, especially in terms of the mechanical properties of the final products.[1,2]

Among all the materials used so far to replace and repair damaged bone tissues, magnesium silicate bioceramics are one of the most promising, thanks to their biocompatibility, osteoinductive properties and good mechanical stability.

In this work, magnesium silicate cement pastes were prepared by hydration of MgO mixed with different SiO2 batches at different Mg/Si molar ratios. Pastes were either moulded or 3D printed to obtain set cements that were then calcined at 1000 ˚C to produce biologically relevant ceramic materials. Both cements and ceramics were characterized by means of X-ray diffraction, while two selected formulations were thoroughly characterized by means of injectability tests, Raman confocal microscopy, scanning electron microscopy, atomic force microscopy, gas porosimetry, X-ray microtomography and compressive tests. The results show that bioceramic scaffolds, namely forsterite and clinoenstatite, can be effectively obtained by 3D printing MgO/SiO2 cement pastes, paving the way towards important advances in the field of bone tissue engineering.[3]



[1] Bonini, M., Journal of Nanoscience and Nanotechnology, 2021, 21, 2778–2792.
[2] Mugnaini G.; Resta C.; Poggi G.; Bonini M., Journal of Colloid and Interface Science, 2021, 592, 430–439.
[3] Tonelli M.; Faralli A.; Ridi F.; Bonini M.; Journal of Colloid and Interface Science, 2021, 598, 24–35.

KN005

PVA-based cryogels to clean artworks: insights into diffusional properties and cleaning mechanism

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Restoration of paintings often involves a cleaning step [1]: dirt accumulated on the surfaces or yellowed varnishes can be removed, to ensure the artwork readability and the conveyance of the artist's original message. However, the cleaning of paintings can be an extremely delicate process: capillary penetration and swelling of the paint layers could lead to paint leaching, pigment loss and, in general, to deterioration of the artwork materials [2]. Therefore, cleaning fluids must be confined in soft and retentive scaffolds, able to adapt to surfaces with different morphologies. Poly(vinyl alcohol) (PVA) - based cryogels showed unprecedented cleaning performances on Modern and Contemporary paintings[3,4]. Cleaning abilities can be related to the gels rheological properties, such as their high adaptability to clotted surfaces. Nonetheless, pores' size and connectivity are expected to play a crucial role, as well. The diffusional properties of gels with different macroporosity were investigated and related to gels cleaning abilities. PVA-based cryogels were obtained by mixing a highly hydrolyzed PVA (H-PVA), with partially hydrolyzed PVAs (L-PVAs, with different molecular weights), or polyvinyl pyrrolidone (PVP). H-PVA/L-PVA and H-PVA/PVP mixtures undergo phase separation in the pre-gel aqueous solutions [4]: both L-PVA and PVP form blobs, whose size depends on the polymer's nature and molecular weight. When the solutions are subjected to freeze-thawing, blobs act as templates and form the micron-sized pores of the final networks. The morphology of gels was observed through Confocal Microscopy, while the nano-scale features were obtained through Small Angle-X-ray Scattering (SAXS) measurements. The diffusional properties of gels were investigated on different length scales: gels tortuosity was calculated by tracking the diffusion of dye molecules through the gels pores, with Fluorescence Correlation Spectroscopy (FCS) measurements. The gels were subsequently loaded with an o/w microemulsion and the diffusion of oil droplets (16 nm ca.) was also evaluated. Finally, the diffusion of sub-micron sized polystyrene fluospheres was calculated through confocal image analysis. Results gave us hints about the gels cleaning mechanism: experiments of dye removal from flat substrates showed how pores connectivity and gels tortuosity could be linked to gels cleaning performances. Further investigations will allow us to adapt gel formulations to specific cleaning tasks, and to predict cleaning abilities depending on the type of materials to be removed.

[1] P. Baglioni et al. Langmuir 25 (15) (2009) 8373–8374.
[2] B. Ormsby et al. Stud. Conserv. 54 (sup1) (2009) 29–41.
[3] N. Bonelli et. al. Coll. Interf. Sci. 536 (2019) 339–348.
[4] R. Mastrangelo et. al. Proc. Natl. Acad. Sci. 117.13 (2020) 7011-7020.

KN006

High efficient Au micro-electrodes and SERS substrates produced by inkJet printing

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Noble metal nanostructures are exploited in a wide range of applications, spanning from electrical [1] and sensors [2,3,4]. Inkjet printing has become a compliant technique for sustainable, solution-processed and cost-effective thin-film fabrication. Still, dedicated, and mutual exclusive implementations need to be satisfied to fulfill different applications, i.e. ink stabilizers could interfere with the sensing response, while the high-temperature sintering performed to enhance conductivity could prevent the use of plastics and/or paper substrates. Inspired by the principles of green chemistry, here we show two novel formulations of Au nanoparticles-based inks for manufacturing nanostructured and conductive thin films by using inkjet printing. Laser Ablation Synthesis in solvent was used as elected technique for clean production of a wide range of colloids.[4,5] Minimal amount of biocompatible additives were also used in order to enhance the colloid stability along the printing process. Different ink formulations, as printed or after thermal sintering, were found to result in tunable conductivity and SERS performance. Our films are a few hundred nanometers thick and show an electrical sheet resistance down to 10.8(±4.1) Ω/square, and remarkable optical properties in terms of SERS activity with enhancement factors as high as 10^7 averaged on the mm^2 scale.

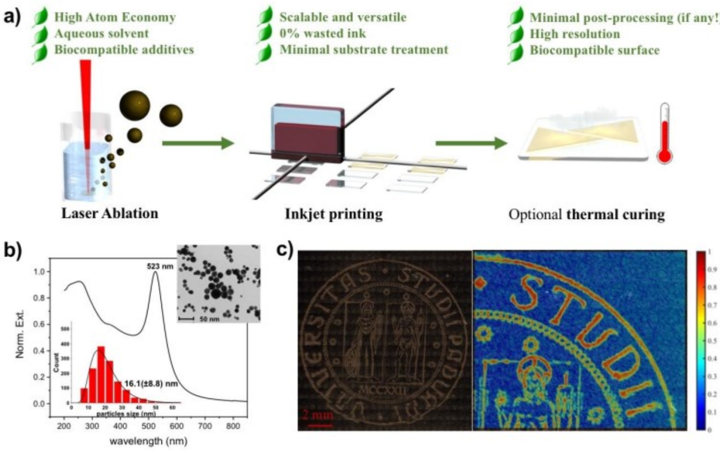

Figure 1: a) artistic representation of the ink production, inkJet printing and sample post-treatment. Each step is designed according to the green-chemistry principles. b) the main component of the inks used in this project are Au nanoparticles, obtained by Laser Ablation Synthesis in water. c) the University of Padova logo was used as model image to show the printing resolution and SERS performance. The dark-field image, on the left, and the µ-Raman false-colored map, on the right, show clear details at the microscale and bright SERS signals

[1] S. Ricci et al. Biosens. Bioelectron. 167 (2020) 112433
[2] L. Litti et al. ACS Appl. Mater. Interfaces 13 (2021) 34752
[3] M. Condorelli et al. Applied Surface Science 566 (2021) 150701
[4] L. Litti et al. Sci. Rep. 10 (2020) 15805
[5] V. Piotto et al. J. Mater. Chem. C 10 (2022) 3819

KN007

Synthetic antiferromagnetic multi-stacks for biomedical applications

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Mesoscale magnetic particles (from few nanometers to microns) are a major class of materials with the potential to revolutionize current clinical diagnostic and therapeutic techniques. They are commonly fabricated by bottom-up chemical methods; however, recent studies have demonstrated that top-down approaches based on techniques developed for micro/nano electronics can be used to fabricate monodisperse magnetic micro/nanoparticles with a complex structure and shape that are hard to obtain by means of chemical routes [1,2]. In this work, thin film stacks consisting of multiple repeats of single $[Co/Pd]_N/Ru/[Co/Pd]_N$ units with antiferromagnetic coupling and perpendicular magnetic anisotropy were investigated and exploited as a potential starting material to fabricate free-standing synthetic antiferromagnetic microdisks [3]. For this purpose, films were directly grown on a sacrificial optical resist layer (AZ5214) spinned on a thermally oxidized Si substrate, which would serve to obtain free-standing particles after its dissolution. Furthermore, the film stack is sandwiched between two Au layers to allow further bio-functionalization. The samples fulfill all the key criteria required for biomedical applications, i.e., zero remanence, zero field susceptibility at small fields and sharp switching to saturation, together with the ability to vary the total magnetic moment (by changing the number of repetitions of the multi-stack) without significantly affecting any other magnetic features. Moreover, the samples show a strong perpendicular magnetic anisotropy, which is required for applications relying on the transduction of a mechanical force through the particles under an external magnetic field, such as the mechanical cell disruption, which is nowadays considered as promising alternative to the more investigated magnetic hyperthermia approach for cancer treatment [4]. Preliminary results on microdisks obtained from the continuous multistacks by electron beam lithography as well as nanosphere lithography approaches are also presented.

[1] T. Vemulkar et al. Appl. Phys. Lett. 110 (2017) 042402
[2] J.G. Gibbs et al. Nanoscale 6 (2014) 9457
[3] G. Varvaro et al., Nanoscale 11 (2019) 21891
[4] Y. Cheng et al. J. Contr. Rel. 223 (2016) 75

KN008

Crossover from individual to collective magnetism: anisotropy vs dipolar interactions in simple and binary dense particle systems

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Dense systems of magnetic nanoparticles may exhibit dipolar collective behavior affecting their performance in various applications. Two fundamental questions remain unsolved: (i) whether the transition temperature may be affected by the particles anisotropy or it is essentially determined by the intensity of the interparticle dipolar interactions, and (ii) what is the minimum ratio of dipole-dipole interaction (E_{dd}) to nanoparticle anisotropy ($K_{ef}V$) energies necessary to crossover from individual to collective behavior. We have studied a series of particle assemblies where dipolar interactions are similarly intense, but the nanoparticle anisotropy widely varies across the series. This parameter has been tuned through different degrees of cobalt-doping in maghemite nanoparticles, resulting in a variation of nearly an order of magnitude. All the bare particle compacts display collective behavior, except the one made with the highest anisotropy particles, which presents "marginal" features. Thus, a threshold of $K_{ef}V/E_{dd} \approx 130$ to suppress collective behavior is derived, in good agreement with Monte Carlo simulations. This translates into a crossover value of ≈ 1.7 for the easily accessible parameter T_{MAX}(interacting)/T_{MAX}(non-interacting) (temperature ratio of the maximum in the temperature dependent zero-field-cooled magnetization of interacting and dilute particle systems), which has been successfully tested against the literature to predict the individual-like/collective behavior of any given interacting particle assembly comprising relatively uniform particles [1].

Secondly, I will show the use of nanoscale-uniform binary random dense mixtures with different proportions of oxide magnetic nanoparticles with low/high anisotropy as a valuable tool to explore or, rather, define the dipolar-collective character of a given magnetic property as that resulting in the collapse of the individual features into a single one due to strong enough interactions. Crucially, such collective character must, in general, be ascribed to specific properties and not to the system [2].

[1] Elena H. Sánchez et al., *Crossover from individual to collective magnetism in dense nanoparticle systems: local anisotropy vs dipolar interactions*, Small (in press, 2022).

[2] Elena H. Sánchez et al., *Simultaneous Individual and dipolar collective properties in binary assemblies of magnetic nanoparticles*, Chem. Mater. 32 (2020) 969.

KN009

Halide Perovskite: an unconventional material for III generation solar cells

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Perovskite solar cells represent a new frontier of 3rd generation photovoltaics. This technology is based on perovskite crystals that have an ABX3 crystalline structure where A is an inorganic or organic cation, B a metal typically Lead or Tin while X a halogen such as iodine or bromine. Thanks to its defect tolerance, high absorption of sunlight, good conduction properties and the ability to be printed directly on a rigid or flexible substrate, perovskite is an excellent material for solar cells and photovoltaic panels with high efficiency and low cost of production. In fifteen years since their discovery, perovskite cells have achieved efficiencies of over 25% and, as far as stability is concerned, they are starting to be comparable to those of conventional photovoltaics. In this talk, I will briefly summarize the fundamental aspects of halide perovskite and its photovoltaic application discussing the advances made in this area at the cell, module and panel levels, also addressing the use of two-dimensional materials such as graphene to improve performance and stability of the cell. Finally, I will present the integration between silicon and perovskite for the fabrication of silicon / perovskite tandem cells which is assuming strategic importance on the national and international scene.

KN010

Synthetic clays as heterogeneous catalysts for degradation of organophosphorus chemical warfare agents simulants

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Chemical warfare agents (CWAs) continue to pose a serious threat to humankind. Alongside conventional countermeasures based on detection, protection and/or decontamination devices and processes, the heterogeneous catalysis represent an increasingly growing method for their treatment, owning to its more sustainable approach to the problem in terms of safety, environment and costs. Synthetic saponite clays, belonging to the 2:1 trioctahedral layered phyllosilicate family, have many interesting properties such as controlled chemical composition, high robustness and adsorption capabilities, good chemical versatility and low production costs, making them excellent catalysts for the abatement of CWAs, as previously demonstrated against the (2-chloroethyl)ethyl sulfide (CEES), a simulant of sulfur mustard.[1,2] On this basis, our research focused on *i*) the preparation of 2D heterogeneous catalysts based on cheap, simple and nanostructured synthetic saponites, and *ii*) their application as effective, safe and sustainable CWAs abatement systems. Several saponite solids were prepared accordingly, through different hydrothermal and/or post-synthesis procedures: 1) as-synthetized (SAP); 2) with niobium centers positioned in the inorganic framework (Nb-SAP); 3) intercalated with proton (H-SAP) and sodium (Na-SAP) cations; 4) in a pillared form, with Fe^{3+}/Al^{3+}-oxide pillars integrated into interlayer space (P-SAP). Commercial non-ordered mixed (Al_2O_3-SiO_2) and niobium (Nb_2O_5) oxides were tested as references. Paraoxon-ethyl and parathion-ethyl, organophosphorus compound widely used as pesticides in agriculture, were selected as anti-cholinergic nerve CWAs simulants, at different concentrations. The catalytic tests were performed in batch glass reactors at 25 °C, 1 bar and in water or anhydrous ethyl acetate, w/o addition of H_2O_2. The reaction was monitored overtime by GC-FID/MS, HPLC, UV-Vis, ^{31}P-NMR, CHN and FTIR techniques. Under anhydrous conditions, saponite solids showed good conversion activities of paraoxon (up to *ca.* 80%) (Figure 1), with comparable results exhibited in aqueous medium. Considering the data obtained, hydrolytic and rearrangement processes, rather than oxidation ones, are the main factors governing the degradation mechanism of the CWAs simulant species analyzed.

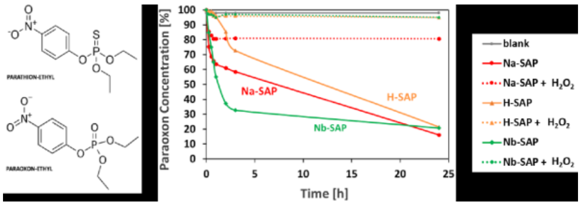

Figure 1: Conversion of paraoxon-ethyl over time, in presence or absence of aq. H_2O_2 1% v/v [H_2O_2/paraoxon molar ratio 5:1]. Conditions: 550 ppm stock solution, anhydrous ethyl acetate, 40 mg catalyst, 25 °C, 1 bar.

[1] F. Carniato, C. Bisio, R. Psaro, L. Marchese and M. Guidotti, *Angew. Chem. Int. Ed.* **2014**, *53*, 10095-10098.

[2] S. Marchesi, M. Guidotti, L. Marchese, C. Evangelisti, F. Carniato and C. Bisio, *Chem-Eur. J.*, **2021**, *27*, 4723-4730.

KN011

Non-conventional peptide self-assembly into a highly conductive supramolecular rope

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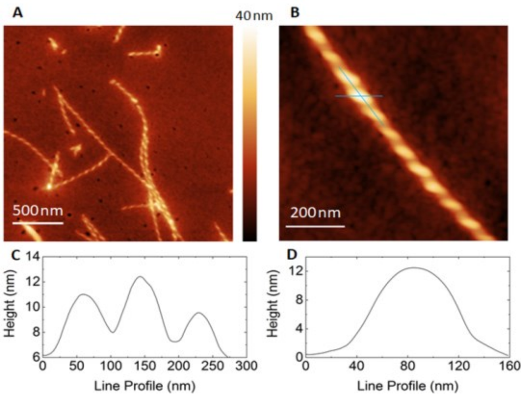
In this work, the conductivity properties of a α,β-peptide, containing three units of *syn* H2-(2-F-Phe)-h-PheGly-OH, able to self-assemble on surface into an innovative and fascinating supramolecular rope is described. This material was characterized by AFM, electronic conduction, and fluorescence measurements. With molecular dynamics simulation, we show that this hexapeptide can self-assemble into antiparallel β-sheet layer, stabilized by intermolecular H-bonds, which, in turn, self-assemble into many side-by-side layers, due to π-π interactions. The peculiarity of the peptide used is that it is composed of alternating α and β amino acids. In comparison with peptides composed of only α- or only β- amino acids, α, β-peptides show greater chemical diversity, giving rise to different secondary structural motifs, which self-assemble into complex structures of controlled geometries. As matter of fact, we demonstrated that in this system, the presence of aromatic residues at the intramolecular interface promoted by the alternation of α,β-amino-acids in the primary sequence, endorses the formation of a super-secondary structure where the aromatic groups are very close to each other, conferring to the system excellent electron conduction properties. This work demonstrates the capability and future potential of designing and fabricating distinctive nanostructures and efficient bioelectronic interfaces based on α,β-peptide, by controlling structure and interaction processes beyond just the ones obtained with only α- or only β-peptides.

Figure. AFM characterization of the peptide supramolecular rope structure.



KN012

Structure and dynamics of a perfluorinated Ce(IV)-based Metal Organic Framework by Solid-State NMR

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In the last decades, metal-organic frameworks (MOFs) have emerged as inorganic/organic hybrid porous materials with exceptionally large surface area. In particular, Ce(IV)-based MOFs have been devised in the last decade to exploit the redox chemistry of this metal in catalysis and photocatalysis [1]. Furthermore, substitution of hydrogen with fluorine atoms in organic linkers has been applied to change the hydrophilic/hydrophobic properties of MOFs. In benzene dicarboxylate ligands (BDC2^{-}) such a substitution modifies the dihedral angle between the carboxylate groups and the phenylene ring, as well as the energy barrier for the phenylene ring rotation [2], thus affecting the MOF properties related to gas capture and storage.

Solid State Nuclear Magnetic Resonance (SSNMR) has established as one of the most powerful techniques for the characterization of structural and dynamic properties at the molecular scale in MOFs [3,4]. In particular, chemical shift values in SSNMR spectra provide local structural information unavailable from other techniques, while 2D homonuclear and heteronuclear correlation experiments can be used to explore spatial proximities between nuclei and, therefore, molecular fragments. Morever, many nuclear observables (anisotropic line shapes, nuclear relaxation times, residual interactions) accessible by SSNMR give unique possibilities for the study of linker motions. In the present work, multinuclear SSNMR is applied to investigate structural and dynamic properties of F4_MIL140A(Ce), a recently synthesized perfluorinated Ce(IV)- based MOF with very good hydrothermal and mechanical stability. The framework is formed by cerium oxide chains units linked by tetrafluorobenzenedicarboxylate (TFBDC2^{-}) linkers giving rise to small pores, which render these materials particularly suitable to CO$_2$ adsorption.

High-resolution ^{19}F-^{13}C cross-polarization (CP) and heteronuclear correlation (HETCOR) SSNMR experiments and ^{19}F direct excitation experiments were exploited to unravel the local environment of crystallographically independent TFBDC2^{-} linkers. Moreover, the interactions of the TFBDC2^{-} ligands with water molecules present in as synthesized F4_MIL140A(Ce) were highlighted by ^{1}H-^{13}C CP experiments. The dynamics of TFBDC2^{-} ligands was instead studied by analyzing the spin-lattice relaxation times (T$_1$) and chemical shift anisotropy of ^{13}C and ^{19}F nuclei as a function of temperature and supporting the SSNMR measurements with DFT calculations.

[1] J. Jacobsen et al., Dalton Trans. 49 (2020) 16551.
[2] A. Gonzalez-Nelson et al., J. Phys. Chem. C 143 (2021) 12053.
[3] Y. Fu et al., Coord. Chem. Rev. 427 (2021) 213563.
[4] C. He et al., Solid State Nucl. Magn. Reson. 117 (2022) 101772

KN013

Thermal and Thermodynamic Stability of Hybrid Organic-Inorganic Perovskites for Photovoltaic Applications

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Since the discovery of the light-harvesting properties of methylammonium lead halides ($CH_3NH_3PbX_3$) in 2009,[1] hybrid organic-inorganic perovskite (HOIP) compounds have been subject to a huge amount of research studies, resulting in ever increasing power conversion efficiencies (up to above 23%). As a consequence, these materials has rapidly become the best candidates as possible substitutes of common semiconductors in photovoltaic cells. However, it became soon evident that the practical use of HOIPs has to deal with the serious drawback of their scarce thermal and thermodynamic stability. For this reason, many variants of the original chemical compositions were proposed with the aim to achieve better stability, both thermal and towards external agents.

In the last few years many experimental and theoretical studies were published addressing the crucial issue of HOPI stability. Here we present the main results obtained by our group using a multi-technique approach which combines thermodynamic and kinetic measurements [2,3] based on X-Ray Diffraction, Knudsen Effusion Mass Spectrometry, thermogravimetry, and differential scanning calorimetry.

On this basis, the prototypical compound $CH_3NH_3PbI_3$ was shown to follow different gas-releasing decomposition paths:

$$CH_3NH_3PbI_3(s) \rightarrow PbI_2(s) + NH_3(g) + CH_3I(g)$$
$$CH_3NH_3PbI_3(s) \rightarrow PbI_2(s) + HI(g) + CH_3NH_2(g)$$

whose competition is sensitive to experimental conditions, such as temperature, evaporation mode (open surface vs. effusion conditions), physical form of the sample. The effects of chemical modifications of the organic cation and of the metal ion are currently under investigation.

[1] A. Kojima et al. J. Am. Chem. Soc. 131 (2009) 6050.
[2] A. Ciccioli and A. Latini, J. Phys. Chem. Lett. 9 (2018) 3756.
[3] A. Ciccioli et al Phys. Chem. Chem. Phys. 21 (2019) 24768.

CO_2 conversion processes over silicate-based systems induced by mechanical milling

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The chemical weathering of silicate-based minerals is a geological natural process which involves CO_2 mineralization at expenses of mafic and ultramafic rocks, and it can drive a mitigation action of atmospheric CO_2 concentration values. Main products of chemical weathering process are metallic carbonates, which can be further subjected to subsequent reduction paths under specific conditions, leading to CO_2 evolution products [1,2]. But notwithstanding the involved chemical processes, thermodynamically favored, can be worthy of potential interest in an ecological transition scenario, however the length of time scale of natural process results in kinetic constraints, which strongly limit the applicative possibilities of the process itself.

Then, the search of proper ways to overcome such limitations attracted the attention of the scientific community, and recent results on a lab scale suggest that the use of external mechanical energy allows to successfully improve the reaction kinetics even under mild conditions [3-5].

Along this line, in the present work we addressed our attention to the mechanochemical processes between CO_2 and different classes of silicates, minerals, pure systems as well as industrial slags.

To this, mechanochemical reactors were suitably developed, to operate either under batch conditions, either under continuous flow of gaseous reagents. The chemical processes, formally occurring at room temperature and atmospheric pressure, are characterized by high conversion and fast kinetics, which, in turn, depend on the specific experimental conditions.

Solid phases and gaseous systems, and their evolution during the chemical processes, were characterized by resorting to several instrumental techniques, with the aim to gain insights of the conversion kinetics and reaction mechanism.

Acknowledgments

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[1] E. H. Oelkers et al., Mineral carbonation of CO2. Elements 4 (2008) 333.

[2] U.S DOE, National Energy Laboratory, CO2 Utilization Focus Area, https://netl.doe.gov/carbon-management/carbon-utilization.

[3] V. Farina et al. Frontiers Energy Research 7 (2019)107.

[4] K. L. Sandvik et al. Adv. Powder Technol. 22 (2011) 416.

[5] F. Torre et al., Powder Technology 364 (2020) 915.

KN015

Functional core- mesoporous shell nanoparticles as photoactive materials

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Core-shell nanostructures consisting of a solid core of functional nanoparticle (NP) and a mesoporous silica shell (MSS) represent versatile generation of nanomaterials able to convey into a single structure multi-functionality useful for applications in different fields including catalysis, adsorption, separation, sensing to biomedicine [1-3]. Superparamagnetic [3], metal [1] NPs with different size, shape or degree of aggregation have been embedded in mesoporous silica structures to combine the magnetic or plasmonic properties of the functional core with the cargo capability of the MSS, characterized by high surface area. Since their first development, different mesophases have been synthesized ranging from hexagonal ordered [4], worm-like disordered, stellate, dendritic and central-radial pores structures [1-3], whose design aims at increasing pore size improving the loading efficiency of large macromolecules and NPs. Here, core structures consisting of plasmonic $Cu_{2-x}S$ NPs with size below 15 nm or spherical non-porous silica NPs embedding luminescent Carbon Dots (C Dots) of about 30 nm have been synthesized and coated with MSS with pore size ranging from 3-4 nm up to tens of nanometers, showing wrinkle-like dendritic and central-radial mesostructures. A soft-template approach has been used to grow the mesoporous structures under basic condition, in the presence of tetraethylorthosilicate (TEOS) using cetyltrimethyl ammonium bromide (CTAB) as surfactant. Monophasic and biphasic soft-template strategies have been explored to modulate the pores structures and the impact of CTAB and TEOS concentration, type of base and organic solvent, has been investigated by a comprehensive morphological, structural and optical characterization. Plasmonic and luminescent mesostructures based on $Cu_{2-x}S$ NPs and C Dots, respectively, have been fabricated and their activity as robust photothermal transducer agents, with additional antimicrobial activity against *Escherichia Coli*, the former, and as optically traceable contrast agent, the latter, demonstrated.

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[1] X. Du, S. Z. Qiao, Small 2015, 11, 392
[2] C. Xu, C. Lei, Y. Wang, C. Yu, Angewandte Chememie International Edition 2022, 61, e202112752
[3] S. Nemec, S. Kralj ACS Applied Materials Interfaces 2021, 13, 1883
[4] F. Rizzi, R. Castaldo, T. Latronico, P. Lasala, G. Gentile, M. Lavorgna, M. Striccoli, A. Agostiano, R. Comparelli, N. Depalo, M. L. Curri, E. Fanizza, Molecules 2021, 26, 4247

KN016

On the relation between structure and functionality during heterogenous catalysis

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X-rays are an ideal probe for studying structural properties of matter and, thanks to the brilliance of synchrotron sources, they are also employed to determine the atomic structure and morphology of surfaces and interfaces.

Surface x-ray diffraction has been originally developed to determine the static structure of surfaces. However with the development of x-ray sources, detectors and analysis tools it is now possible to explore in detail processes which occur at surfaces.

Aim of this talk is to present our results dealing with the in-situ characterisation of the structure and morphology of a catalyst during a surface reaction. The case study is the heterogenous catalytic oxidation of CO on Pd single crystal surfaces [1,2] and on supported nanoparticles [3,4] at ambient pressure and real temperatures.

Our studies point the role of the surface oxide in boosting the reaction rate [4].

References
[1] R. van Rijn et al., Phys. Chem. Chem. Phys. 13 (2011) 13167
[2} B.L. Hendriksen et al., Nat. Chem. 2 (2010) 730
[3] O. Balmes, et al., Phys. Chem. Chem. Phys. 14 (2012) 4796
[4] W.G. Onderwaater et al., Catalysis, Structure & Reactivity 3 (2017) 89

KN017

Computational studies of the reactive pathways leading to the parasitic release of singlet oxygen in metal-air batteries.

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Aprotic metal-oxygen batteries are a novel and intriguing concept in applied electrochemistry. These systems are variants of the so-called Li-air batteries and up to now are in their research infancy. The redox chemistry of these batteries is not entirely understood, but it is clear that the superoxide disproportionation reaction is a crucial step for their operation in aprotic solvents. In the best scenario, it leads to peroxide formation while in the worse one, it releases singlet molecular oxygen. In this presentation I will summarize the results of several recent computational works [1-4] where we have addressed the fundamental mechanisms of metals superoxide disproportionation and the thermodynamics of such reaction for alkali (Li, Na and K) and alkaline earth (Be, Mg and Ca) containing systems, using multiconfigurational ab-initio methods.

In particular, I will report the results of these computations on the electronic properties of the peroxide MO_2^- trimer that reveal the competition between the expected reactive path leading to peroxide and an unexpected reaction channel that involves the reduction of the alkaline ion. Both channels lead to the release of triplet and singlet O_2 and to solvated neutral metal atoms. The formation of these species, even in small amounts, might have a negative impact on the performance of aprotic metal-O_2 batteries given their well-known reducing activity and high reactivity towards protic impurities and oxygen-bearing molecules.
The role of redox mediators such as I_2 and Br_2 (often used to lower overpotentials) has also been explored and their role in selecting particular reactive pathways will be also discussed.

[1] A. Pierini, S. Brutti and E. Bodo Superoxide Anion Disproportionation Induced by Li+ and H+: Pathways to $^1O_2$ Release in Li-O_2 Batteries, ChemPhysChem, 21, (2020) 2060–2067
[2] A. Pierini, S. Brutti and E. Bodo, Reactive pathways toward parasitic release of singlet oxygen in metal-air batteries, npj Computational Materials 7, (2021) 126
[3] A. Pierini, S. Brutti, and E. Bodo, Study of the Electronic Structure of Alkali Peroxides and Their Role in the Chemistry of Metal–Oxygen Batteries, J.Phys. Chem. A, 125, (2021) 9368–9376
[4] A. Pierini, S. Brutti, and E. Bodo, Reactions in non-aqueous alkali and alkaline-earth metal-oxygen batteries: a thermodynamic study, Phys. Chem. Chem. Phys., 23, (2021) 24487-24496

KN018

Earth abundant semiconductors and materials efficient deposition for inorganic thin film solar cells

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The recent 6th IPCC report on how to mitigate climate change highlights solar cells as being the most effective and cheapest way of reducing greenhouse gas emissions. Our calculations show that for a northern European country like Luxembourg to go 100% renewable, approximately 4% of the land surface is required to be covered in solar cells. Given the urgent need to deploy large areas of photovoltaic panels, any chosen technology must consist of earth abundant elements, be stable for decades, and be fabricated using low energy materials efficient deposition methods. Thin film inorganic solar cells can fit these criteria and we will demonstrate our research in both the p and n-type layers of these devices.

Many thin film inorganic solar cell technologies currently being researched are based on a p-n junction. The first n-type layer adjacent to the p-type layer is normally based on cadmium sulfide, where the cadmium is rare and toxic, and the layer is normally deposited using a chemical bath where most of the chemicals end up in solution or on the walls of the chamber rather than in the device. We have recently developed a replacement Zn(O,S) earth abundant non-toxic alternative buffer layer deposited by inkjet printing which reduces solvent and chemical waste by several orders of magnitude. The method allows the deposition of uniform layers of controlled thickness with tuneable opto-electronic properties depending upon the annealing conditions. Using this deposition method we have achieved device efficiencies similar to and better than the reference.

Solar cells based on the p-type $Cu(In,Ga)Se_2$ semiconductor now achieve light to electric power conversion efficiencies similar to that of commercial polycrystalline silicon solar cells and the energy required to fabricate the solar cell is considerably lower. However, indium is relatively rare and this will stop its use in large scale deployment if $Cu(In,Ga)Se_2$ is used in the traditional large area thin film format. An alternative format which does allow for large scale deployment is the micro concentrator solar cell, where microscale $Cu(In,Ga)Se_2$ islands are illuminated with light concentrated by large area lenses. Not only is the amount of indium reduced by the same factor as the light concentration, but also the efficiency of the devices increases by 2% absolute with every decade of light concentration. Our laboratory focuses on fabricating these micro-devices using materials efficient electrochemical deposition methods.

KN019

R&I in Photovoltaics is key to the Green Energy Transition

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In order to tackle climate change and achieve carbon neutrality by 2050, a deep and immediate transformation of the global energy supply chain is mandatory. Energy is responsible for about three quarters of the global greenhouse gas emissions, most of which are caused by the use of fossil fuels. Renewable energy sources are the obvious solution and highly industrialised countries like Germany or Italian regions like Emilia Romagna have already committed to cover 100% of their energy demand with renewables by as early as 2035.

However, despite photovoltaics (PV) and/or wind are already the cheapest sources of energy in large part of the globe, any plan to meet this ambitious and yet inescapable target requires a massive and coordinated effort, similar to the “man on the moon” mission 50 years ago. As in the case of the moon landing, R&I are key to enable and accelerate the process by filling the gaps between knowledge, industry, policy and society.

Besides being inexpensive and efficient, PV is a fundamental part of the solution because it is implementable at all scales, from the giga-solar-farms for utility scale generation, to kW-size rooftop installations, and has the potential to contribute to a large fraction of the overall (local and global) energy demand with no additional impact on land consumption[1].

In order to unlock this huge potential, a R&I strategy, ranging from materials science to energy and socio-economic systems, must be defined and implemented at all TRLs including fundamental research.

This work illustrates the contribution of the Italian PV Network of R&I, towards this objective[2], within the frame of the SET Plan and thanks to the support of PV-IMPACT, a Horizon2020 CSA devoted to the implementation of the SET Plan objectives and targets.

The results obtained over the last 5 years and the future opportunities for the research community will be presented and discussed in the context of the European and international scenarios.

[1] Mazzer, M., Moser, D., 2021. How solar energy could power Italy without using more land. Nature Italy. https://doi.org/10.1038/d43978-021-00048-z

[2] Bizzarri, F., Moser D., Mazzer, M. et al, 2020. A Strategic Plan for R&I to Relaunch the Italian PV Sector and Contribute to the Targets of the National Energy and Climate Plan, https://pvimpact.eu/news-resources/reports/download/a-strategic-plan-for-research-and-innovation-to-re

KN020

The challenging spectroscopy of molecular bricks of life in the gas-phase

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High-resolution molecular spectroscopy in the gas-phase provides accurate information on intrinsic molecular features without any perturbation from non-innocent environments. Furthermore, these techniques allow for the unequivocal identification of chemical species in hostile environments, e.g. the interstellar space and planetary atmospheres, but also in gaseous samples of unknown composition. However, medium-sized molecules like the molecular bricks of life (e.g., DNA bases or amino acids) are already challenging systems because of the increased dimension and/or flexibility with respect to small semi-rigid species. From the experimental point of view, both features lead to the congestion of spectral lines, thus preventing a straightforward assignment and interpretation of the results. Thanks to terrific developments in both software and hardware in the last decades, computational spectroscopy has become an invaluable tool for the disentanglement of spectroscopic features. However, both the dimensions of the systems and the need of exploring flat potential energy surfaces, prevent the brute force use of very accurate, but very expensive state-of-the-art quantum-chemical methodologies. Based on these premises, although several studies of biomolecule building blocks have been performed, the computational characterization of potential energy surfaces is usually restricted to limited systematic searches of energy minima employing geometries (when not also energies) of limited accuracy. These approaches do not allow the a priori prediction of the spectroscopic outcome, but only its a posteriori interpretation in terms of the agreement between experimental and computed spectroscopic parameters for a reduced number of conformers, which are not necessarily the most stable ones. In this latter case, the a posteriori analysis might lead to misleading interpretation, with any unbiased disentanglement of the conformational landscape becoming impossible. Based on these premises, I will analyze the current status and perspectives of a new strategy we are developing for the fully a priori prediction of the spectral signatures of medium-sized molecules in the gas phase with special reference to rotational and vibrational spectroscopy of some representative molecular bricks of life [1-3].

[1] V. Barone, C. Puzzarini, G. Mancini, *Integration of Theory, Simulation, Artificial Intelligence and Virtual Reality: A Four-Pillar Approach for Reconciling Accuracy and Interpretability in Computational Spectroscopy*, Phys. Chem. Chem. Phys. 23,17079-17096 (2021).
[2] V. Barone, S. Alessandrini, M. Biczysko, J. R. Cheeseman, D. C. Clary, A. B. McCoy, R. J. DiRisio, F. Neese, M. Melosso, C. Puzzarini, *Computational Molecular Spectroscopy*, *Nature Rev. Meth. Primers* 1, 38 (2021).
[3] V. Barone, M. Fusè, S. M. Vieira Pinto, N. Tasinato, *A computational journey across nitroxide radicals: from structure to spectroscopic properties and beyond*, MOLECULES 26, 7404 (2021)

KN021

Oral Contributions

Relative binding free energies between chemically distant compounds using a bidirectional nonequilibrium approach

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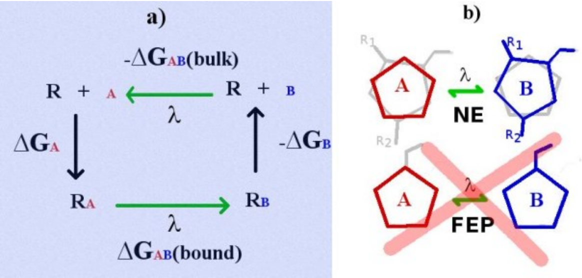
In the context of advanced hit-to-lead drug design based on atomistic Molecular Dynamics simulations, we propose a dual topology alchemical approach for calculating the relative binding free energy (RBFE) between two chemically distant compounds. The method (termed NE-RBFE) relies on the enhanced sampling of the end-states in bulk and in the bound state via Hamiltonin Replica Exchange, alchemically connected by a series of independent and fast nonequilibrium (NE) simulations. The technique is an extension our recently proposed NE-based protocol[1,2] for absolute binding free energy calculations in drug-receptor systems and has been implemented in a bi-directional fashion, applying the Crooks theorem to the NE work distributions for RBFE predictions. The dissipation of the NE process, negatively affecting accuracy, has been minimized by introducing a smooth regularization based on shifted electrostatic and Lennard-Jones non bonded potentials. As a challenging testbed, we have applied our method to the calculation of the RBFE's in the recent host-guest SAMPL9 international contest, featuring a macrocyclic host with guests varying in the net charge, volume and chemical fingerprints. Closure validation have been succesfully verified in cylces involving compounds with disparate Tanimoto coefficient, volume and net charge. NE-RBFE is specifically tailored for massively parallel facilities and can be used with little or no code modification on most of the popular software packages supporting nonequilibrium alchemical simulations such as Gromacs, Amber, NAMD or OpenMM. The proposed methodology bypasses most of the entanglements and limitations of the standard single topology RBFE approach for strictly congeneric series based on free energy perturbation (FEP), such as slowly relaxing cavity water, sampling issues along the alchemical stratification and the need for highly overlapping molecular fingerprints. By affording the calculation of the RBFE for chemically distant (or scaffold-hopping-related) compounds in a matter of few hours on a HPC facilities, NE-RBFE has the potential to become a powerful tool in the last stages of the computer-based hit-to-lead drug discovery pipeline in industrial settings.



[1] M Macchiagodena, M Pagliai, M Karrenbrock, G Guarnieri, F Iannone, P .Procacci*, J. Chem theory Comput, 2020, 16 , 7160-7172

[2] M Macchiagodena, M Karrenbrock, M Pagliai, P Procacci*, J. Chem. Inf. Model, 2021, 61, 5320-5326

[3] P Procacci, Curr. Op. Struct. Biol. , 2021, 67, 127-134

OR001

Covalently interconnected TMD networks via defect-engineering for high-performance electronic devices

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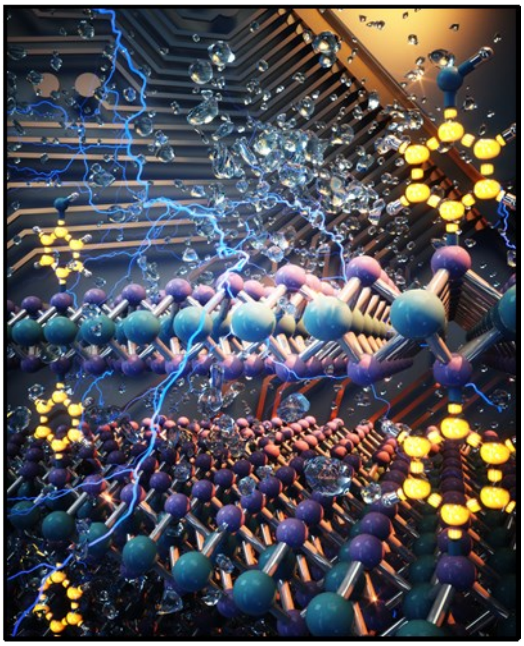

Figure 1: Illustration of network formation in MS_2 thin-films by means of π-conjugated dithiolated molecules.

Solution-processed semiconducting transition metal dichalcogenides (TMDs) are at the centre of an ever-increasing research effort in printed (opto)electronics[1]. However, device performance is limited by structural defects resulting from the exfoliation process and poor inter-flake electronic connectivity. We developed a new molecular strategy to boost the electrical performance of TMD-based devices *via* the use of dithiolated π-conjugated molecules, to simultaneously heal sulfur vacancies in solution-processed transition metal disulfides (MS_2) and covalently bridge adjacent flakes, thereby promoting percolation pathways for the charge carrier transport[2]. Our approach represents a radically new and universal functionalization method capable of improving the performance of devices based on solution-processed MS_2 for large-area electronic applications. In particular, we implemented our strategy in liquid-gated thin-film transistors, boosting their main figures of merit by one order-of-magnitude and reaching state-of-the-art electrical performance characterized by competing field-effect mobilities and current ratio, along with the fastest switching time reported to date for devices of this kind[3]. Moreover, covalently interconnected MS_2 networks show additional unique features, such as improved water stability and mechanical robustness. Finally, as a result of an appropriate molecular design of the bridging linkers, one might endow the networks with various functionalities, tuning their properties on-demand according to the ultimate applications.

[1] Wang et al. Nat. Nanotechnol. 7 (2012) 699
[2] Ippolito et al. Nat. Nanotechnol. 16 (2021) 592
[3] Kelly et al. Science 356 (2017) 6

OR002

Time-resolved core level photoemission to reveal transient lattice distortions in transition metal dichalcogenide crystals

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Transition metal dichalcogenides (TMDs) are layered materials with a set of compelling properties, such as strong absorption in the visible region and high carrier mobility, which make them of particular interest for photovoltaics. Moreover, the observation of photo-induced semiconductor-to-metal (2H-to-1T') transitions in TMDs recently allowed creating phase-patterned homojunctions [1], paving the way for the development of novel 2D devices. For both applications, an extensive characterization of optically excited TMDs is a fundamental requirement.

In this contribution, we present the time-resolved X-ray photoemission study of a semiconductive 2H-$MoTe_2$ crystal performed at the ANCHOR-SUNDYN endstation [2] of the Elettra Synchrotron (Trieste). Upon photoexcitation, we observe a long-lived (> 1 µs) core level shift to lower binding energies that is due to the formation of surface photovoltage fields. Interestingly, in the sub-nanosecond range the photoemission peaks shift to the opposite direction, thus suggesting the presence of a distinct physical process at shorter timescales. With the support of DFT calculations, we modelled the deformation of the $MoTe_2$ lattice in the out-of-plane direction, which is along the pathway for the 2H-1T' phase transition. Our data indicate an intermediate lattice excitation state with a measured lifetime in the order of 600 ps, in which the displacement of Mo and Te atoms causes the core photoelectrons to shift to higher binding energies.

These results show that high-resolution time-resolved photoemission, combined with suitable theoretical simulations, is a valuable tool for studying not only the electronic and chemical modifications of photoexcited systems, but also lattice distortions and phase transitions.

[1] S. Cho, S. Kim et al. Science 349 (2015) 625
[2] R. Costantini, M. Stredansky, et al., J. Electron Spectros. Relat. Phenomena 229 (2018) 7

OR003

In-silico prediction of the organic solar cells' efficiency

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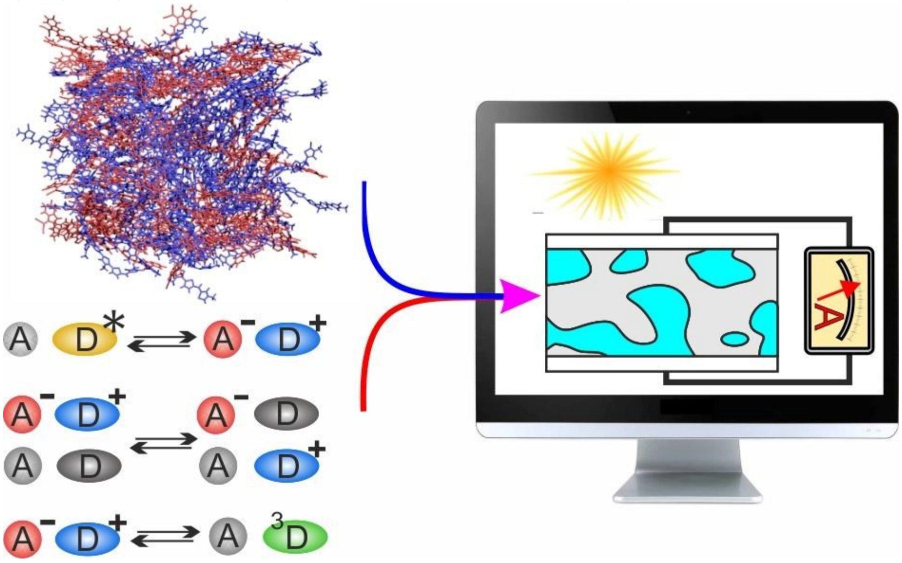
Non-fullerene acceptors led to outstanding improvements in the efficiency of organic photovoltaic devices, with high promises of further advancements [1]. Several studies have been performed to rationalise their exceptional performances, with the final goal of developing a reliable protocol for the identification of new materials with better properties. In this respect, we here combine molecular dynamics, density functional theory and Fermi's Golden Rule (FGR) [2] to model two recent all-small-molecule bulk heterojunctions with high power conversion efficiencies, namely ZR1:IDIC-4Cl and ZR1:Y6 [3]. We evaluate the FGR rates for photoinduced hole and electron transfer, excitation energy transfer, and charge recombination on a statistical ensemble of donor/acceptor pairs extracted from molecular dynamics simulations. Our results provide a simple rationalisation of the great performance of Y6: aside from a slower charge recombination rate, we found that the charge transfer state for ZR1:Y6 can be accessed both via electron and hole transfer, while the latter pathway is significantly slower for IDIC-4Cl, indicating that its first excited state behaves as a trap, as confirmed by a simple kinetic model. In light of the recently reported possibility of developing donors and acceptors with complementary absorption spectra, multiple photoexcited charge transfer pathways represent a key property to efficiently harvest the whole solar spectrum [4].



[1] Y. Lin et al. ACS Energy Lett. 5 (2020) 2935; G. Hedley et al. Chem. Rev. 117 (2017) 796
[2] V. Barone et al. Phys. Chem. Chem. Phys. 15 (2013) 3736; R. Borrelli et al. Wiley Interdiscip. Rev. Comput. Mol. Sci. 3 (2013) 542
[3] R. Zhou et al. Nat. Commun. 10 (2019) 5393
[4] A. Landi et al. J. Mater. Chem. A 9 (2021) 24849; A. Landi et al. ACS Appl. En. Mater. submitted

OR004

Experiments-guided modeling of MCM-41: pores symmetry impact on gas adsorption

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Meso- and microporous materials are characterized by exceptionally high specific surface area, for which they are successfully exploited in the design of sorbents for a wide range of applications, such as gas sweetening, wastewaters treatment and air pollutants removal [1-4]. Silica-based mesostructured materials, such as MCM-41, are particularly interesting for the narrow pore size distribution and different possible post-synthetic functionalization routes. Complementary experimental techniques allow correlating sorption efficiency to surface chemistry and material morphology. Surprisingly, porous sorbents are often modeled as simple flat surfaces [5] or slits [6], or accurate studies are performed at the local level [7], without taking pore's radius, curvature, density, and symmetry into account. Although spatial arrangement of the pores is considered in many reports, symmetry and wall thickness are sometimes unrealistic [8]. The present study aims at building a reliable 3D model of MCM-41 by exploiting experimental results from state-of-the-art characterization techniques as input for computational modeling. From low-angle x-ray diffraction techniques (LA-XRD), lattice parameter could be determined to characterize the 2D hexagonal porous order. Solid-state NMR was applied to retrieve the atomic ratio between bulk and surface Si atoms. N_2-adsorption-desorption isotherms were measured and analyzed with different theoretical models, namely, BET, to estimate the specific surface area, and either BJH or DFT, to obtain the pore size distribution. From lattice parameter and average pore diameter, wall thickness was estimated. The application of these different theories, however, generally leads to significantly different results, and which one should be used for the different materials is still an open point. In addition, although the typical space group symmetry of MCM-41 is the hexagonal p6mm, preparation of mesostructured silica materials with tetragonal p4mm symmetry was reported [9,10]. Thus, we built models with 2 different pore size and 2 different symmetries. By combining classical Molecular Dynamics and Grand Canonical Monte Carlo simulations, experimental adsorption isotherm was reconstructed. Thermodynamics of the adsorption was quantified through ΔG, ΔH and ΔS, together with trajectory analysis to characterize adsorbed layers in terms of intermolecular and solid-gas interactions, and gas molecules order parameters. The collected evidence allowed to obtain a 3D computational model reflecting all the available experimental results, opening the route to further investigation. The impact of the pore size and mesopores symmetry was revealed at the microscopic level.

[1] C. Cara et al. J. Mater. Chem. A 5 (2017) 21688
[2] L. Mafra et al. Chem. Eng. J. 336 (2018) 612
[3] A. Gallo-Cordova et al. Sci. Total Environ. 711 (2019) 134644
[4] M. Sanna Angotzi et al. Nanoscale Adv. 3 (2021) 6100
[5] S. Kwon et al. ACS Appl. Mater. Interfaces 9 (2017) 31683
[6] J. Cao et al. AIChE J. 65 (2019) e16733
[7] L. Mafra et al. J. Am. Chem. Soc. 139 (2017) 389
[8] A.A. Sizova et al. Colloids Surf. A 524 (2017) 87
[9] C. Jin et al. Angewandte Chemie 48 (2009) 9268
[10] L. Han et al. Chem. Mater. 24 (2012) 504

OR005

Density Functional Theory study on the electronic properties of a novel TPA and PTZ-based hole transport material and its interfacial features with MAPI perovskite

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Since 2009, the photovoltaic community has been devoted great research efforts to perovskite solar cells (PSCs) leading to power conversion efficiency above 25.5%. However, the lack of long-term stability of devices is one of the main barriers hampering large-scale PSCs commercialization and it can be mainly imputable to the degradation of PSCs components. In particular, the PSCs stability largely depends on the HTMs and their interface contact with the perovskite, which are key points to address to promote further development of this technology in terms of efficiency and stability [1]. In this context, this contribution dissects the structural and the electronic properties of a novel triphenylamine (TPA) and phenothiazine (PTZ)-based HTM (HTM1), as well as the mutual polarization effects when it interacts with the (001) surface of the parent MAPI perovskite. To this end, Density Functional Theory (DFT) methods have been employed, comparing the results with those of the state-of-the-art Spiro-OMeTAD and an efficient recently designed TPA and PTZ-based HTM, *i.e.* PTZ2 [2]. Our findings reveal that HTM1 possesses all the well-known electronic properties to be considered a valid HTM candidate and its hole mobility could outperform those of the other HTMs considered here [3,4]. Additionally, it has good adhesion properties with the MAPI surface, which results in structural modifications and bonds formation at HTM1/MAPI interface. Nevertheless, our results also point out the lack of a sufficient driving force for the hole transport, suggesting that the binding motif is not the only parameter influencing the charge transport process, while the perovskite composition can also strongly affect it. Indeed, MAPI perovskite was inadequate when combined with TPA and PTZ-based HTMs, supporting its limited employment for real devices’ fabrication [4,5].

[1] M. Vasilopoulou et al. Chem. Soc. Rev. 49 (2020) 4496-4526.
[2] R. Grisorio et al. ACS Energy Lett. 2 (2017) 1029–1034.
[3] C. Coppola et al. Materials Chemistry and Physics 278 (2022) 125603.
[4] C. Coppola et al. Submitted manuscript (2022).
[5] L. A. Castriotta et al. Submitted manuscript (2022).

OR006

Fibroin and nanocellulose composite films as new adhesives for aged textiles

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While historical and aged textiles (canvas, silk) constitute a relevant portion of our Cultural Heritage, there is a lack of physico-chemically compatible solutions to provide re-adhesion to the damaged fibers at the micro-scale without introducing potentially harmful adhesives such as those based on synthetic polymers.

Colloidal systems and advanced functional materials based on biopolymers are optimal candidates to fill this gap. We recently investigated composite dispersions of self-regenerated silk fibroin (SRSF) or SRF and cellulose nanocrystals (CNC), to cast adhesive films able to recover the mechanical properties of aged silk fibers [1,2]. SRSF produce films with controlled crystalline/amorphous content depending on the protein concentration in the dispersion; however, there is a limit to the concentration for the sole SRSF dispersions, as crystalline SRSF phases (with scarce chain mobility) cast over aged silk fibers produce brittle films that worsen the fibers' mechanical behavior. Amorphous SRSF films instead improve the flexibility of the aged textiles [1]. Adding CNC to the dispersions speeds up the assembly of SRSF likely thanks to protein organization on the cellulose fibers, and composite films with partially crystalline fibroin (high -helices content) can be cast even at low fibroin concentration. Noticeably, the composite films produce better improvement than the sole SRSF amorphous films or CNC films obtained from dispersions with the same concentration of consolidant [2].

The hybrid SRSF-CNC dispersions candidate thus as new promising adhesives for aged silk (and canvas) textiles; in addition, we provided for the first time a semi-quantitative evaluation of the structuring effect of CNC on SRSF assemblies, which can help the development of "green" chemistry solutions in different fields even beyond Cultural Heritage preservation, such as biomaterials and tissue engineering, and the preparation of composites with enhanced properties.

[1] D. Chelazzi et al. J. Colloid Interface Sci. 576 (2020) 230-240
[2] C. Cianci et al. Colloids Surf. A 634 (2022) 127944

OR007

Synergistic effects and emerging properties in nanoparticle interaction with membrane cholesterol

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Accounting up to 50% of mammalian plasma membrane lipids, cholesterol is one the most biologically relevant membrane constituents in the study of membrane interactions with exogenous agents. Membrane cholesterol performs numerous physiological functions, including modulating bilayer fluidity, which is vital to most cellular processes, and promoting membrane bending during membrane fusion processes. Lipid membrane fusion is a critical component for a large number of biological events, e.g. synaptic transmission, subcellular cargo transport, and viral infection. Small amphiphilic gold nanoparticles (AuNPs) capable of passively and non-destructively entering plasma membranes have emerged as interesting synthetic agents with tailored functionalities for diagnostic and therapeutic purposes. Remarkably, these NPs have also recently been shown to promote calcium-triggered fusion of biological vesicles in a manner similar to much more complex endogenous protein structures [1]. Still, the molecular details underlying this fusogenic behaviour – and in particular the role of cholesterol in the presence of NPs – have yet to be explored. In this work, we aim to elucidate how cholesterol-tuned membrane fluidity affects the passive uptake of amphiphilic AuNPs into the lipid bilayer of plasma membranes and how this interaction reflects on the nanoparticles' fusogenic activity. To this purpose, we synthesised monodisperse AuNPs with an average size of 2.4 nm and protected by a mixed monolayer of hydrophobic and ω-charged alkylthiols [2,3]. On the membrane side, we focused on fluid-state phosphocholine (PC) vesicles containing biologically relevant percentages of cholesterol (0÷40 mol %). These biomimetic membranes composed of PCs – the main plasma membrane components – have established themselves as reliable models for studying, at the molecular level, passive physicochemical interactions involving the plasma membrane bilayer. By combining quartz crystal microbalance experiments, atomic force microscopy, fluorometric assays and molecular dynamics simulations, we show that membrane cholesterol hinders the molecular mechanism for passive penetration of AuNPs within PC bilayers, resulting in a dramatic reduction in the amount of membrane-embedded AuNPs [2], but at the same time significantly enhances their peculiar fusogenic ability. Taken together, our results provide an original contribution to the mechanistic understanding of the interaction between plasma membranes and amphiphilic AuNPs, paving the way for new discoveries and technological innovations in the use of such fusogenic nanomaterials in next-generation nanomedicine.

[1] M. A. Tahir et al. PNAS 117 (2020) 18470
[2] E. Canepa et al. J. Phys. Chem. Lett. 12 (2021) 85833
[3] E. Canepa et al, Nanoscale 12 (2020) 19746

OR008

Molecular orbital theory in cavity QED environments

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Many ground breaking works have shown that the strong light matter coupling achieved inside optical cavities can significantly impact molecular properties all the way from the modification of absorption and emission spectra to the alteration of photochemical processes. Inside a cavity, the photonic vacuum couples to molecules creating polaritonic states with distinct features. Most importantly, the properties of the mixed matter-photon states can be engineered tuning the photonic part of the system, which means that polaritons represent a very effective way to modulate matter properties in a non-invasive way. A detailed theoretical description of the strong coupling regime is urgently needed to develop an intuitive picture of cavity chemistry and the first ab initio methodologies to model these light matter systems have been proposed just recently. To ease the rationalization of cavity induced effects we introduce a new ab initio method, strong coupling quantum electrodynamics harthree fock (SC-QED-HF) leading to the first fully consistent molecular orbital theory for strongly coupled systems. Our framework is non-perturbative and allows us to display the modifications of the electronic structure due to the interaction with the photon field. In particular, we show that the orbitals obtained using SC-QED-HF can be used to predict the reactivity inside optical cavities studying an SN2 reaction and we confirm that electrons interacting with the quantized field get more localized, in this way reducing the electronic dipole in the electric field direction. We also pinpoint classes of systems for which we expect significant cavity effects and investigate the importance of cavity induced electronic effects in vibrational strong coupling regime. Finally, we tackle the problem of molecular ionization in optical cavities showing that the presence of the quantized field introduces correlation between the free electron and the ionized system. We develop a theoretical framework to study these systems and show that the inclusion of the free electron is critical to describe ionization processes in QED environments.

[1] Riso, R.R. et al. Nat. Commun. 13, 1368(2022).
[2] Riso, R.R. et al. ArXiv preprint arXiv:220306050(2022).

OR009

The morphology and the electro-optical properties of PDLCs cured in the presence of electric fields

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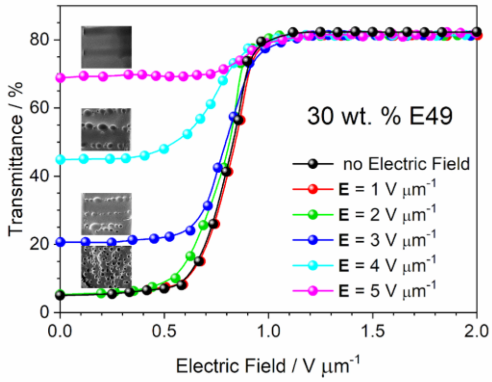
Polymer Dispersed Liquid Crystals, PDLCs, are composite materials generally formed by spherical liquid crystal droplets embedded in a polymer matrix. Reports of PDLCs with different droplet shape are not widespread. In this work epoxy/LC mixtures in different weight ratios were polymerised in the presence of an external AC electric field with increasing strengths. The morphology and the electro-optical properties of the obtained PDLCs were found to be dependent from the strength of the electric field applied during the curing process. Common PDLCs with spherical droplets were obtained from samples polymerised under the action of low strength electric fields, but PDLCs with elongated droplets and memory states were found for polymerisation performed in the presence of intermediate electric fields. For larger electric fields, PDLCs were characterised by a morphology with long cylindrical channels and large memory states [1].



[1] A. Tursi et al. Liq. Cryst. In press (2022)

Strategies to simulate dephasing-assisted quantum transport with digital quantum computers

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Simulating charge and energy transfer in extended molecular networks requires an effective model to include the environment because it significantly affects the quantum dynamics. A prototypical effect known as environment-assisted quantum transport (ENAQT) consists in the enhancement of the transfer efficiency by the interaction with an environment [1]. A simple description of this phenomenon is obtained by a quantum master equation describing a quantum walk over the molecular network in the presence of inter-site decoherence. We have considered the problem of simulating the dynamics underlying ENAQT in a digital quantum computer [2] and introduced two different quantum algorithms. The first one based on stochastic Hamiltonians [3] and the second one based on a collision scheme [4]. We have tested both algorithms by simulating ENAQT in a small molecular network on a quantum computer emulator and provided a comparative analysis of the two approaches (Figure). Both algorithms can be implemented in a memory efficient encoding with the number of required qubits scaling logarithmically with the size of the simulated system while the number of gates increases quadratically. We found that the algorithmic quantum trajectories generated by the two simulation strategies realize distinct unravellings of the site-dephasing master equation. In our approach, the non-unitary dynamics of the open system is obtained through effective representations of the environment, paving the way to digital quantum simulations of quantum transport influenced by structured environments.

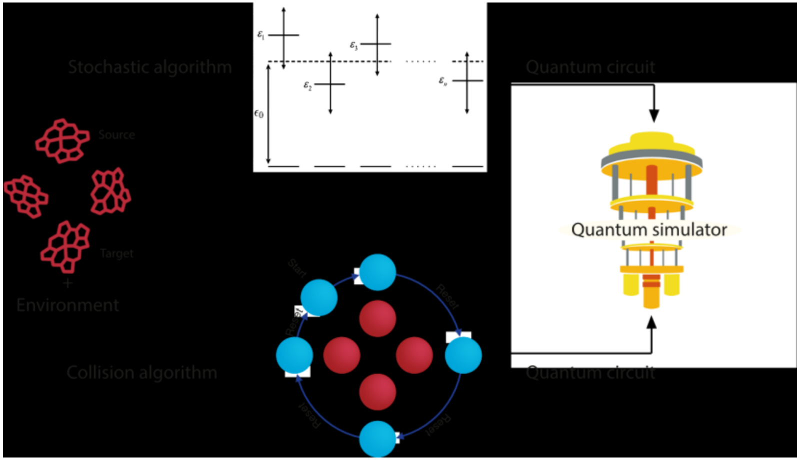

Figure. The transport problem is mapped into our Stochastic or Collision algorithms, then translated into a quantum circuit that is executed by a quantum computer simulator.

[1] M. Mohseni et al. J. Chem. Phys. 129 (2008) 174106
[2] F. Gallina et al. New J. Phys 24 (2022) 023039
[3] K. Gaab et al. J. Chem. Phys. 121 (2004) 7813
[4] G. García-Perez et al. npj Quantum Inf. 6 (2020) 1

OR011

A spectroscopic approach to the diagnosis of Heart-Failure in a rat model

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The investigation of biological tissues is generally performed with techniques that involve a morphological characterization through an optical microscope. These procedures require specific pre-treatments and the use of exogenous labeling compounds that could alter the function of a target molecule or the state of cells and tissues due to physical or chemical interactions. For this reason, finding an alternative experimental approach that allows an accurate, label-free and chemically specific analysis of biological samples is of primary importance. Spectroscopic techniques represent an ideal candidate to fulfill these requirements: most of them don't require labeling agents and are fast and not expensive. In particular, Fourier- transform infrared (FTIR) and Raman scattering techniques can be powerful tools to characterize the physiological or pathological state of the tissue [1,2]. In recent years, the spectroscopic investigation of biological samples has mostly focused on the diagnosis of several types of cancers and neurological disorders [3], but other pathologies affect the lives of millions of people in the world. Heart failure (HF) is a major clinical challenge that is associated with a markedly high risk of death. It affects over 26 million people worldwide, accounts for the majority of hospitalizations among the elderly, and its prevalence continues to rise. In addition, metabolic diseases such as obesity, diabetes, and hypertension often contribute to the development of HFpEF [4]. The challenging diagnosis of HFpEF is often belated and the treatment of this condition remains largely unsuccessful, with a five-year survival rate of 43% after a first diagnosis [5]. In this work, we perform an ex-vivo analysis of both hearts and kidneys of rats to detect early cardiac and renal biochemical alterations due to HFpEF progression and to evaluate the effect of innovative pharmacological treatments. Promising results are presented and discussed.

1. M.J. Baker et al. Nat Protoc. 9 (2014) 1771
2. H.J. Butler et al. Nat Protoc. 11 (2016) 664
3. V. Balan et al. Materials 12 (2019) 2884
4. R. Altara et al. Front. Endocrinol. 8 (2017) 160
5. C. Tribouilloy et al. Eur. Heart J. 29 (2008) 339

OR012

Theoretical study of functionalized based silica-based mesostructured sorbents for gas sweetening

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The importance of CO_2 as anthropogenic greenhouse gas and its impact on the environment is well established. The so-called Carbon Capture and Utilization (CCU) strategies continue to attract much attention, both for environmental and for economic reasons [1,2]. Silica-based mesostructured materials are particularly interesting to design efficient and selective adsorbents for CO_2, due to the possibility of obtaining a highly ordered 2D arrangement of pores with a narrow size distribution. In addition, these materials can be tailored by proper functionalization. For instance, it has been demonstrated that an improvement of selectivity and adsorption capacity is provided by amine groups, even at low pressure and in the presence of moisture [3,4].

By properly designed atomistic models and computer simulations, it is possible to capture the microscopic details underlying the selectivity and efficiency of the sorption process. The aim is to extend the present knowledge and improve our capability of designing technologically improved materials for specific applications and operative conditions.

This study is focused on the sorption of CO_2/CH_4 mixtures with different composition and at different operative conditions (P,T) inside the network of silica-sorbents mesopores. Particular attention is paid to the pore size and the surface density of the functional groups. We combine classical Molecular Dynamics and Grand Canonical Monte Carlo simulations to reconstruct the adsorption isotherms and to assess selectivity and capacity as a function of mixture composition. The evaluation of the total and partial molar ΔG, ΔH and ΔS, together with the analysis of the trajectories at the microscopic level to characterize the adsorbed layers in terms of composition, intermolecular and solid-gas interactions, and gas molecules order parameters, shed light on synergistic or antagonistic effects among the gas molecules during the sorption process. The mesostructured silica-based sorbents are investigated both in the absence (only surface silanol groups) and in the presence of surface grafted amine moieties. When needed, DFT calculations are performed to investigate pertaining reactions leading to chemisorption. In addition, the role of moisture is investigated. Not only thermodynamics aspects of the sorption are evaluated, but also the diffusion of the gas molecules inside the mesostructured pores network is studied, in order to obtain a more complete picture in terms of gas permeability through these silica-based materials.

[1] S. Choi et al. ChemSusChem 2 (2009) 796-854
[2] R. Ben-Mansour et al. Applied Energy 161 (2016) 225-255
[3] L. Mafra et al. Chem. Eng. J. 336 (2018) 612-621
[4] A.D. Ebner et al. Ind. Eng. Chem. Res. 50 (2011) 5634–5641

OR013

Multivariate Metal–Organic Framework/Single-Walled Carbon Nanotube Buckypaper for Selective Lead Decontamination

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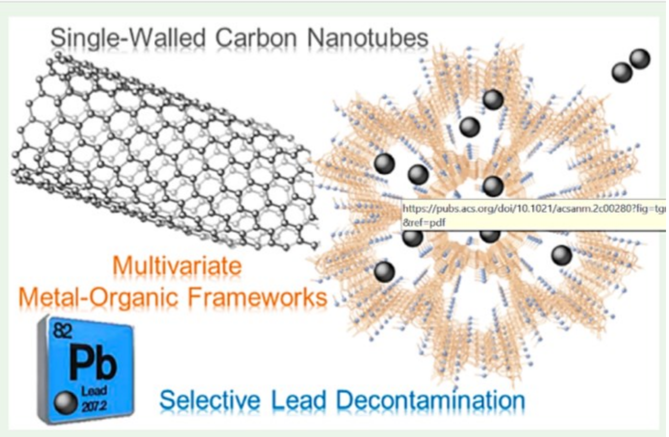
The search for efficient technologies empowering the selective capture of environmentally harmful heavy metals from wastewater treatment plants, at affordable prices, attracts wide interest but constitutes an important technological challenge. We report here an eco-friendly single-walled carbon nanotube buckypaper (SWCNT-BP) enriched with a multivariate amino acid-based metal–organic framework (MTV-MOF) for the efficient and selective removal of Pb^{2+} in multicomponent water systems. Pristine MTV-MOF was easily immobilized within the porous network of entangled SWCNTs, thus obtaining a stable self-standing adsorbing membrane filter (MTV-MOF/SWCNT-BP). SWCNT-BP alone shows a moderately good removal performance with a maximum adsorption capacity of 180 $mg \cdot g^{-1}$ and a considerable selectivity for Pb(II) ions in highly concentrated multi-ion solutions over a wide range of lead concentration (from 200 to 10000 ppb). Remarkably, these features were outperformed with the hybrid membrane filter MTV-MOF/SWCNT-BP, exhibiting enhanced selectivity and adsorption capacity (310 $mg \cdot g^{-1}$, which is up to 42% higher than that of the neat SWCNT-BP) and consequently enabling a more efficient and selective removal of Pb^{2+} from aqueous media. MTV-MOF/SWCNT-BP was able to reduce [Pb^{2+}] from the dangerous 1000 ppb level to acceptable limits for drinking water, below 10 ppb, as established by the current EPA and WHO limits. Thus, the eco-friendly composite MTV-MOF/SWCNT-BP shows the potential to be effectively used several times as a reliable adsorbent for Pb^{2+} removal for household drinking water or in industrial treatment plants for water and wastewater lead decontamination.



[1] M. Baratta et al. ACS Appl. Nano Mater. (2022), in press.

OR014

Thermoelectric and magnetic properties of Co_2ZrSn and Co_2HfSn Heusler alloys

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Half-metallic ferromagnetic alloys are attracting considerable interest for their potential applications in spintronic devices. Since the development of spin-voltage generators is regarded as crucial in spintronics, thermoelectric properties are also of high interest for such technology, having been proved spin-Seebeck effect to be an effective way to generate and carry spin-polarized current over relatively long distances. Co-based Heusler alloys are considered to be among the most promising classes of half-metallic compounds as they combine suitable magnetic, electronic and transport properties with compositional versatility and high thermal stability. Also, several Co-based Heusler alloys were found to be suitable for spin-injection processes due to their semiconductive-like band gap located in one of the two electronic sub-bands. Thus, half-metallic alloys which show a constant, relatively large Seebeck coefficient (when compared with other thermoelectric materials) and a high Curie temperature (possibly above room temperature) are greatly looked after.

In this work, Co_2ZrSn and Co_2HfSn Heusler alloys were studied by combining experimental and ab-initio investigations in order to accurately estimate their electronic density of states in proximity of the Fermi level and to measure their transport properties over a wide range of temperatures. The effect of secondary phases which are typically present in this type of alloy [1] was also taken in account. The thermoelectric properties were determined both for compounds in which the amount of such impurities is negligible and for samples with secondary phases content up to 20% in weight. The effect of these on the transport properties is discussed in detail. In particular, an increase of electrical conductivity was observed for the spurious alloys, which translates on an increase of power factor. On the contrary, the Seebeck coefficient is overall not greatly influenced by the presence of impurities.

[1] Yin, Ming, Song Chen, and Philip Nash. "Enthalpies of formation of selected Co2YZ Heusler compounds." Journal of alloys and compounds 577 (2013): 49-56.

OR015

Aprotic Electrolytes with Lithium Salts in Li-O_2 batteries: characterization via experiments and Polarizable Molecular Dynamics

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The innovations that are occurring in many strategic industrial sectors towards green technologies heavily rely on the constant improvements of energy storage devices. Aprotic lithium-oxygen batteries (aLOBs) are the so-called-generation 5 energy storage devices and will displace current technologies in the mid-term. aLOBs can outperform current lithium-ion batteries in terms of theoretical energy density (about 3500 Wh/kg vs 150 Wh/kg), and can disclose outstanding improvements also in terms of costs and safety.[1] Despite these fascinating opportunities, many missing pieces are still preventing these systems from achieving their theoretical figures, as aLOBs suffer from low round-trip energetic efficiency, poor reversibility and materials instability. One of the most important drawbacks that affects aLOBs is the degradation of electrolyte components (salts, organic solvents, redox mediators) during the discharge and charge processes.

The aim of this communication is to illustrates innovations in materials design for Li-O_2 battery systems from experimental and theoretical perspectives. More precisely, theoretical calculations employing a polarizable force field, AMOEBA[2], have been used to simulate the bulk conditions of the solvent and to obtain information the dynamical and transport properties of the electrolyte. The need to use a polarizable force field lies in the requirement to accurately represent the chemical surroundings of the (charged) electrolyte. From the experimental side we present new measurements of the conductivity and transport numbers of lithium in solutions as well as Raman spectra that can aid the characterization of the solvation state of the electrolyte and that can be directly compared with the calculation. The combination of the results of theory and experiments will be used as the basis for future calculations and provide guidelines for designing of aprotic electrolyte solutions for Li-oxygen batteries.

[1] B. Scrosati, K. M. Abraham, W. Van Schalkwijk, J. Hassoun. *Lithium Batteries. Advanced Technologies and Application.* New Jersey. Wiley. 2013

[2] Ponder JW, Wu C, Ren P, et al. *Current Status of the AMOEBA Polarizable Force Field*. J Phys Chem B. 2010, 114, 2549–2564.

OR016

ITI-a versatile visible light activated photoswitch

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Multi-responsive molecular photoswitches are fundamental building blocks for achieving user-defined control of the properties and functions of chemical and biological systems. We have deeply analysed the photochemistry and photoswitching ability of a new class of fully-visible-light-operated molecular photoswitches, Iminothioindoxyls (ITIs)[1]. ITIs show an unprecedented band separation of over 100 nm, isomerize on the picosecond time scale and thermally relax on the millisecond time scale. Using a combination of advanced spectroscopic and computational techniques, we provide the rationale for the switching behavior of ITIs and the influence of structural modifications and environment, including aqueous solution, on their photochemical properties. We furthermore explore the acidochromism of ITIs, showing that protonation of the thermally stable *Z* isomer leads to a strong batochromically-shifted absorption band, allowing for fast isomerization to the metastable *E* isomer with light in the 500-600 nm region [2]. By controlling the acid-base equilibrium which determines the populations of protonated and neutral forms of the *E* isomer, we are able to modulate its half-life the over three orders of magnitude, increasing it from milliseconds up to tens of seconds. Finally, starting from a computationally-supported design, we developed Phenylimino Indolinone (PIO), a green-light addressable T-type photoswitch, showing negative photochromism, and reverting the isomer stability observed for the parent molecule ITI [3].

[1] Hoorens M.W.H et al, (2019) *Nature Communications*, *10*, 2390
[2] Medved' M., et al (2021) *Chemical Science*, 12 (12), pp. 4588-4598.
[3] Crespi, S., et al (2021), Angewandte Chemie - International Edition, 60 (48), 25290-25295

OR017

Study on the structure *vs* activity of designed non-precious metal electrocatalysts for CO_2 conversion

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The rising level of carbon dioxide (CO_2), mainly a consequence of human activities, is leading to devastating consequences to our environment and has raised concerns in public opinion. To face this issue, governments are working to reduce CO_2 emissions, whilst the scientific community is focusing on implementing the electro-chemical conversion of CO_2 (CO2RR) as a source of added value chemicals. Due to the high stability of the CO_2 molecule, to make its conversion practical, the process requires a suitable electrocatalyst. With the aim to understand the mechanism toward specific CO_2RR products and thus increase selectivity, in this study, we have explored copper-based nanoparticles (Cu NPs) as one of the most promising catalysts for CO_2 conversion[1] and investigated the reactivity as a function of selected experimental parameters. The results were rationalized via theoretical investigation, which will also be discussed, to understand the mechanism behind their activity but, most importantly, to relate structure to selectivity. The Cu NPs, prepared via an unconventional sol-gel process[2,3], were shown to be pure, homogeneous in size and morphology, and showed a total FE above 90% toward CO_2RRs. The higher FE toward the production of C_2H_4 (up to 33% at an applied potential of -1.0 V) is one of the highest FE reported so far for Cu, without using expensive support or co-catalysts. The final products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and elemental mapping (EDX).

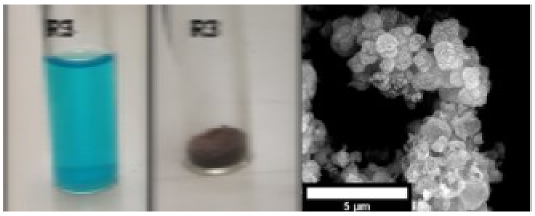

Figure 1. a) Cu-Urea complex in solution, b) corresponding products after heat treatment and c) SEM of Cu particles.

[1] A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, Energy & Environmental Science, 2010, 3.
[2]C. Giordano, C. Erpen, W. Yao, B. Milke and M. Antonietti, Chem. Mater., 2009, 21, 5136-5144.
[3]T. Rao, W. Yuan, N. Jeyachandran, A. G. Nabi, D. Di Tommaso and C. Giordano, ChemRxiv, 2021.

Polarizable force field for Bio-compatible Ionic Liquids

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Ionic liquids and deep eutectic solvents have increasingly attracted a huge research effort due to their application in many fields of technology like solvents, catalyst or electrolytes [1,2]. In recent years it has been assessed that the “green” nature of ionic liquids is a complex question, realizing that most of them are toxic and less environment-friendly than supposed.[3]

The very recent implementation of ionic liquids based on choline and ammino acids (AAILs) is particularly relevant for their intrinsic biocompatibility. Despite their growing use in many technological setups, the physico-chemical mechanism in which AAILs interact with biological matter is still largely unknown [3].

Polarizable molecular dynamics simulations represent a powerful tool for understanding these mechanisms and provide a “best balance” option between the accuracy of ab-initio that is too computational demanding to sample adequate timescale and classical parametrized dynamics which is too simple to accurately model electrostatic interactions. Some of the crucial ingredients of the interaction energy in ionic liquids are polarization and induction, so that the simulations of dynamical processes in ionic liquids has long been recognized by the community to need an electrostatic model as accurate as possible. Due to ionic nature of the materials, these effects are particularly important, and they will affect dynamic quantity like fluidity, ionic mobility or conductivities which are all heavily underestimate by non-polarizable models [4].

New polarizable force field parameters have been determined and especially designed to describe the nanoscopic behavior of AAILs and this new force field can be considered an extension of AMOEBA model to biocompatible AAILs. It has been parametrized with high quality ab-initio data and is able to accurately reproduce the structure and the interaction energies.

The new force field can be used to gain a detailed understanding of the bulk structure and dynamics of AAILs and to rationalize in which way these systems act as solvents of biomolecules.

[1] Stettner, T.; Balducci, A. Energy Storage Mater (2021) 40, 402– 414
[2] Xu, P.; Liang, S.; Zong, M.-H.; Lou, W.-Y. Biotechnol. Adv (2021), 51, 107702
[3] Kumari, P.; Pillai, V. V. S.; Benedetto, A. Biophys. Rev. (2020), 12, 1187– 1215
[4] Bedrov, D.; Piquemal, J.-P.; Borodin, O.; MacKerell, A. D.; Roux, B.; Schröder, C. Chem. Rev. 2019, 119, 7940– 7995

OR020

Magnetically levitated protein corona as a physical tool for cancer detection

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Personalized protein corona (PPC), *i.e.*, the protein shell that coats nanoparticles once in contact with clinically relevant body fluids, has recently emerged as a detection means of tumor onset [1]. However, the huge number of experimental steps typically required for the characterization of nanoparticles' PPC can affect the reproducibility and inter-laboratories consistency of the experimental data [2]. To overcome such limitation, herein we exposed an indirect characterization approach that exploits the magnetic levitation (MagLev) of PPCs derived from 15 healthy individuals and 30 oncological patients affected by four cancer types, *i.e.,* breast cancer, prostate cancer, colorectal cancer, and pancreatic ductal adenocarcinoma (PDAC). Briefly, using MagLev device, we analyzed levitation profiles of PPC-coated graphene oxide (GO) NPs that migrate along a magnetic field gradient in a paramagnetic medium (Figure 1). Our investigation demonstrates that the sensitivity and specificity of the PPC-based MagLev tool depend on the cancer type with the global classification accuracy ranging from 70% for prostate cancer to a notable 93,3% for PDAC.

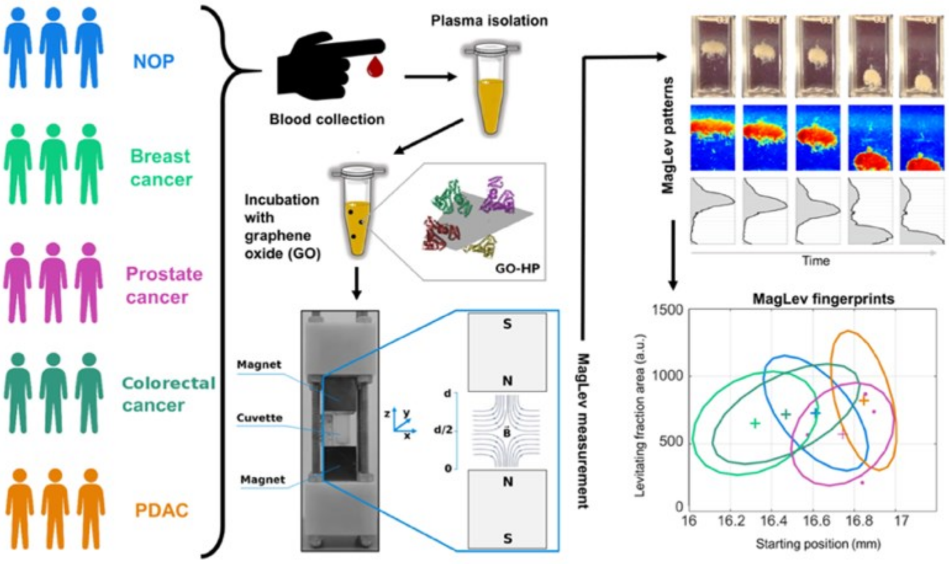

Figure 1. *The experimental workflow includes (i) blood collection from healthy and oncological donors, (ii) plasma isolation and incubation with graphene oxide (GO), (iii) injection of GO-protein complexes in paramagnetic solution, (iv) sample inserting in Maglev device for proteins magnetic levitation, (v) image acquisition and processing, and (vi) identification of cancer fingerprints.*

[1] R. Di Santo et al., *Frontiers in bioengineering and biotechnology*, *8* (2020) 491.
[2] L. Digiacomo et al., *Cancers*, *13*(20) (2021) 5155

OR021

From the structural characterization of rhamnolipids mixture to the eco design of green formulations

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The study of the dynamic nano-structuring of components in solution is the physico-chemical basement for formulation design. Surfactants are key components in a plethora of industrial formulations. On the flipside, because of their scarce biodegradability and toxicity, synthetic surfactants constitute an environmental issue worldwide.

In this direction the investigation of biosurfactant properties represent the essential conditions for the rational design of innovative formulations in accordance to the new trend of sustainability in the eco-transition framework.

Biosurfactants, amphiphiles produced by bacteria, yeast and plants, represent a valid alternative to synthetic ones, allowing a reduction of environmental and potential health problems [1]. Besides satisfactory functionality as solubilizers, emulsifiers, wetting and foaming agents, biosurfactants present good tolerance to temperature and pH changes and, above all, fast biodegradability and low toxicity.

Rhamnolipids, glycolipids electively produced by *Pseudomonas aeruginosa* as secondary metabolites, are among the most promising biosurfactants for practical applications. Specifically, rhamnolipids can be proposed as suitable candidates to totally or, at least, partially replace anionic surfactants in several industrial formulations. For this reason, the investigation of their mixtures with largely employed synthetic surfactants is strategic. In this contribution, we compare the physico-chemical and functional properties of a commercial rhamnolipid sample in aqueous solution with those of sodium lauryl ether sulfate (SLES), an anionic surfactant massively used in laundry and household cleaning detergents as well as in personal care and consumer products. The mixtures of these two anionic surfactants are also investigated, analyzing weather, and to what extent, synergistic/antagonistic interactions alter the system behavior with respect to that of the single components. Surface tension, DLS, conductometric and spin-probe EPR results, quantitatively analyzed in terms of molecular-thermodynamic models, show a weak antagonistic behavior which however does not hamper the formation of prolate mixed micelles which co-exist with vesicles. Contact angle measurements, emulsification and foaming tests demonstrate that rhamnolipids can effectively replace up to 90 wt% of SLES with negligible effects of the functional behavior. On the other hand, the ecotoxicity of these surfactant mixtures is very low, nominating rhamnolipids as key components of next-generation green formulations.

[1] R. Esposito et al. Nanomaterials 11 (2021) 331

OR022

Conductive polymer coating for photosynthetic bacteria in biohybrid devices

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Conductive polymer layers on the surface of several bacterial species have been used to intercept and funnel outside the cells the electron flow produced by microbial metabolism and transfer them in an electronic circuit of a biohybrid device. Photosynthetic purple nonsulfur bacteria are anoxygenic microorganisms with versatile metabolism, as they use sunlight to oxidize a broad variety of organic compounds in addition to heterotrophic and photoautotrophic alternative metabolisms [1,2]. The strain R26 of the bacterium *Rhodobacter (R.) sphaeroides* was coated with a melanin-like material to improve the interface between electrodes and photosynthetic microorganisms.

Polydopamine (PDA), produced by self-assembly of dopamine, is a very versatile and bioinspired polymer which has found widespread applications mostly due its ability to adhere and cover surfaces of different chemical composition. The oxidative conditions employed for the formation of this dark insoluble polymer are mild and biocompatible and have inspired scientists to develop novel nanomaterials for optoelectronics [3,4].

Biocompatibility of dopamine was tested by its addition in the growth media [5] of metabolically active cells *R. sphaeroides.* Furthermore, the ability of these monomers to self-assemble and polymerize in the bacterial growth medium was considered one of the requirements of the polymer to be used as coating material beside the tunable conductive properties and the flexible structure. The effects of dopamine concentration on the light-induced photoresponse of the biohybrid systems will be thoroughly discussed.

[1] G. Buscemi et al. Advanced Materials Technologies 7 (2) (2022) 2100245
[2] G. Buscemi et al. Photochemistry (2021) 385-410
[3] G. Buscemi et al. ACS Applied Materials & Interfaces under revisions
[4] F. Milano et al. Advanced Functional Materials 29 (21) (2019) 1805521
[5] D. Vona et al. MRS Advances 5 (18-19) (2020) 957-963

OR023

Aggregation of Gold Nanoparticles Induced by Halide Salts

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Metal nanoparticles exhibit unique optical properties due to their interaction with electromagnetic fields, known as Surface Plasmon Resonance (SPR). This is dependent on the environment as well as their size, shape and aggregation state [1]. Gold nanoparticles (Au NPs) have been proposed for applications in a wide range of fieldsapplications including sensing, medicine, photonics and many others. Their SPR can be tuned by changing their shape into e.g. nanorods, nanoplates or nanostars. Alternatively, SPR can be tuned by controlling their aggregation.

In this study, we present the controlled aggregation of Au NP prepared by laser ablation in liquids (LAL) by addition of halide salts. We observe that adding a halide salts induces the formation of a new SPR band that is significantly red-shifted from the initial one (see figure 1), due to the formation of Au NP aggregates, as observed by electron microscopies, and supported by Finite-difference time-domain simulations. We investigated a broad range of factors influencing the kinetics and the extent of the aggregation process, such as initial NP concentration, halide concentration, temperature, and presence of oxygen. The surface composition of such aggregates will be investigated.

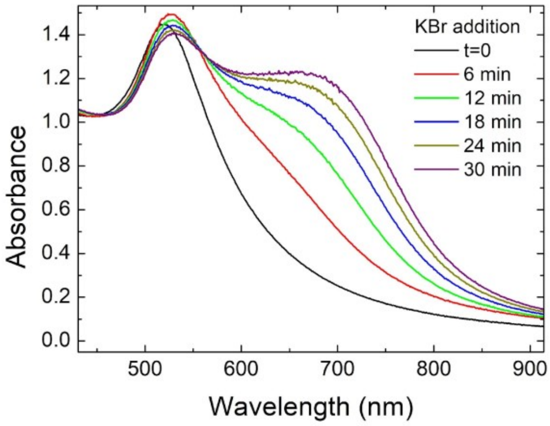

Figure 1. Time evolution of absorption spectraum of Au NPs by addition of KBr (left) and simulated spectra of Au NP chains of different lengths (right)

[1] Trugler, A. Optical Properties of Metallic Nanoparticles; Springer: Berlin/Heidelberg, Germany, 2016
[2] Fedlheim, D.L.; Foss, C.A. Metal Nanoparticles: Synthesis, Characterization, and Applications; CRC Press: Boca Raton, FL, USA, 2001; p. 352.

OR024

Systematic Computational Scrutiny of the Chalcogenoxide Elimination Panorama

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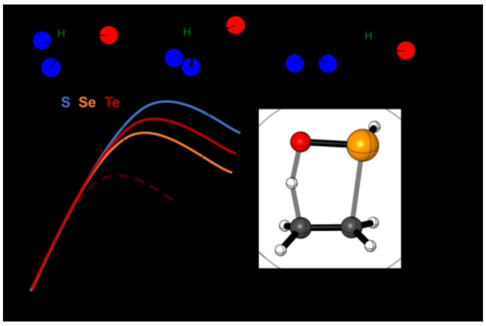
The reactivity of the chalcogenoxide (X=O, with X=S, Se, Te) bond is well-known and exploited in organic chemistry. Indeed, the *selenoxide elimination* (see figure) is one of the most famous organoselenium reactions, because it easily occurs even below room temperature, providing a green way to form carbon – carbon double bonds. For this reason, it has a impactful and multifaceted scope in organic synthesis, biological and toxicological chemistry.[1,2] The same reaction is known for sulfoxides and telluroxides alike, with selenoxide being the best eliminating system.[1,3] In this work, we provide a systematic mechanistic analysis of the reactivity of chalcogenoxides via a properly-benchmarked DFT protocol (ZORA-M06/TZ2P-ae // ZORA-OPBE/TZ2P), employing three different molecular models encompassing minimal systems of theoretical as well as synthetic and biological interest. In addition, different chalcogen oxidation states are considered, i.e. besides "true" chalcogenoxides, in which the chalcogen is in the oxidation state (OS) 0, the elimination chemistry of the OS +2 and OS +4, corresponding to chalcogeninic and chalcogenonic acids, is included in our investigation. These last species also possess a X=O bond that might promote an elimination reaction in a biological environment. The role of the chalcogen (S, Se, Te) and of the OS (0, +2, +4) on the reaction is quantified and rationalized within the framework of the Activation Strain Model of chemical reactivity, to pinpoint how the nature of the chalcogenoxide affects its reactivity. The outcome, among others, is the computational validation of an old hypothesis[3] explaining the surprising kinetic inertia towards elimination of telluroxides with respect to selenoxides.[4]



[1]J. Młochowski, R. Lisiak, H. Wójtowicz-Młochowska, *Organoselenium and Organotellurium Oxidation and Reduction*, Wiley, New York City, **2011**.
[2]R. Masuda, R. Kimura, T. Karasaki, S. Sase, K. Goto, *J. Am. Chem. Soc.* **2021**, *143*, 6345–6350.
[3]S. Uemura, S. Fukuzawa, *J. Am. Chem. Soc.* **1983**, *105*, 2748–2752.
[4]A. Madabeni, S. Zucchelli, P. A. Nogara, J. B. T. Rocha, L. Orian, *manuscript submitted*.

OR025

Mechanical response and yielding transition of silk-fibroin and silk-fibroin/cellulose nanocrystals composite gels

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The development of sustainable biomaterials and green composites is at the forefront of the research efforts in materials science. In this regard, silk fibroin, that is an abundant natural protein produced by silkworms and spiders, have the advantage of presenting a high mechanical strength, which is indeed of interest for applications as biomaterial and in composites. We recently proposed the use of dispersions of self-regenerated silk fibroin (SRSF) extracted from Bombyx mori for the consolidation of fragile silk fibers [1,2]. To further increase the spectrum of fine adjustment of the mechanical properties of the dispersions, and thus better meet the needs of silk conservators, SRSF was blended with cellulose nanocrystals (CNC) [3]. The composition and processing conditions of the composite fibroin gels investigated in the few studies reported in the literature are typically very diverse and specifically tailored towards desired applications: it is thus difficult to draw any general conclusion on the effect of the addition of nanocellulose on the mechanical behavior of these systems. Moreover, mechanical characterization was mainly focused on the measurement of linear viscoelasticity and viscosity, while the yielding transition of the materials remained essentially unexplored. Such transition is of primary interest for processing and application purposes. To fill this knowledge gap, we compare in this work the mechanical response of gels formed by pure SRSF dispersions and by SRSF/CNC mixtures with the same content of SRSF. By combining different rheological techniques and analysis methods, we determine the viscosity and stiffness of the gels, and we characterize in great detail the yielding transition. Our findings show that the addition of CNC alters the gelation kinetics, leads to stronger gels and qualitatively modifies the yielding behavior. In addition, by applying the sequence of physical processes (SPP) approach [4,5] to the analysis of large amplitude oscillatory strain (LAOS) measurements, we find evidence of a broad yielding transition for both gels, that is characterized by a progressive fluidization for which we precisely determine the characteristic strain at which this process starts and the one at which it is almost complete. Our study [6] shows that a detailed analysis of the mechanical properties and yielding behavior of complex gel structures, like those formed by SRSF/CNC dispersions, is of fundamental importance to design adequate processing conditions in several applicative fields.

[1] D. Badillo-Sanchez et al. Polym. Degrad. Stab. 157 (2018) 53
[2] D. Chelazzi et al. J. Coll. Interf. Sci. 576 (2020) 230
[3] C. Cianci et al. Coll. Surf. A 634 (2022) 127944
[4] S.A. Rogers Rheol. Acta 56 (2017) 501
[5] G.J. Donley et al. Non-Newton. Fluid Mech. 264 (2019) 117
[6] G. Poggi et al Coll. Surf. A 636 (2022) 128121

OR026

Thermally activated delayed fluorescence in condensed phase: the role of dielectric and conformational disorder

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Spin recombination statistics impose a limit on the quantum efficiency of organic light emitting devices (OLED), as most of generated excitons are in a non-emissive triplet state. Thermally activated delayed fluorescence (TADF) is a process where a reverse inter-system crossing (RISC) converts dark triplets into bright singlets, raising the theoretical efficiency of OLED up to 100%.
The guidelines for the chemical design of TADF emitters are well known: electron donor and acceptor units are connected in a twisted conformation to minimize the singlet-triplet gap, while intramolecular vibrations allow for non-negligible spin-orbit coupling and transition dipole moment. In OLED, however, emitters are dispersed in amorphous organic matrices, that profoundly affect the photophysics of TADF. If properly understood, the emitter-environment interaction can be exploited to optimize the device in a *smart matrix approach*.
In this work, we take a step in this direction. We exploit an effective model parametrized on first principles calculations to estimate the rates of processes relevant to TADF, using an approach that fully accounts for the non-adiabaticity of molecular vibrations and conformational modes.[1,2] The environment acts in two ways: (a) producing a dielectric response, that can be partitioned into dynamic and static components, and (b) hindering the conformational relaxation of the emitter. The intricate behavior observed in time resolved fluorescence measurements[3] is properly simulated when both effects are modeled, tracing the origin of time-dependent spectral shifts and long-time non-exponential decay to the interplay between dielectric and conformational disorder in the macroscopic sample.

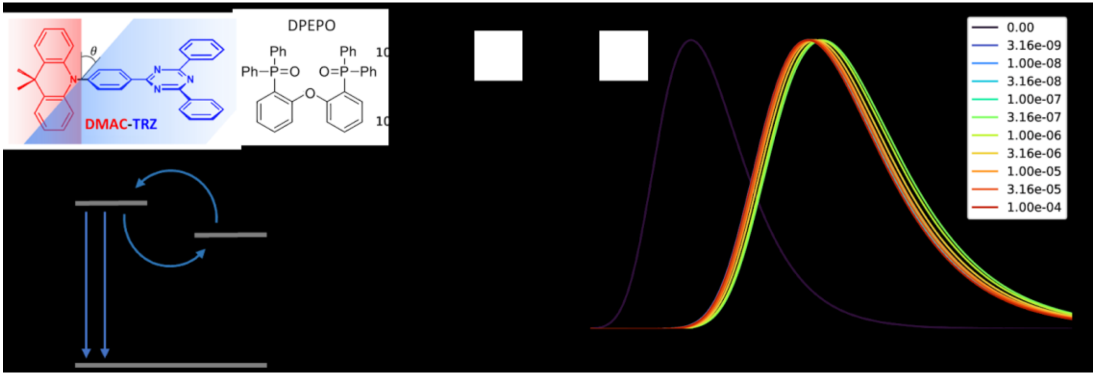

Figure: Sketch of the TADF process. Calculated emission decay and time-resolved emission spectra of DMAC-TRZ in DPEPO matrix.

[1] R. Dhali, D. K. A. Phan Huu, F. Bertocchi, C. Sissa, F. Terenziani, A. Painelli, Phys. Chem. Chem. Phys., 2021, 23, 378-387
[2] D. K. A. Phan Huu, S. Saseendran, A. Painelli, J. Mater. Chem. C, 2022, 10, 4620-4628
[3] K. Stavrou, L. G. Franca, A. P. Monkman, ACS Appl. Electron. Mater. 2020, 2, 9, 2868–2881

OR027

Metal-organic crystals: shaping, uniformity and symmetry breaking

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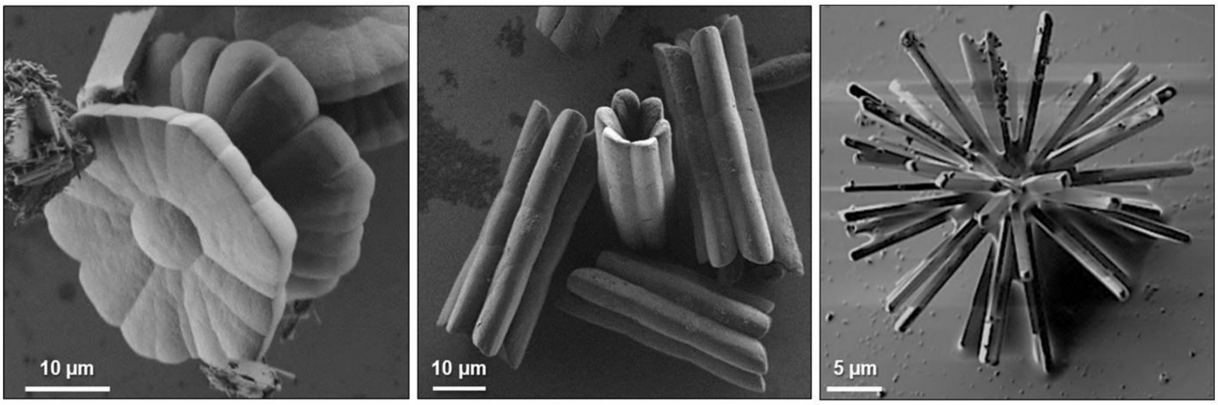
The relationship between crystallization conditions, crystal structure and properties is a pivotal point in chemistry both for the investigation of fundamental aspects and for applications. The interest spans from the macro- to the nanoscale and the range of natural, laboratory-made, organic and inorganic systems. [1] Typically, micro-nano crystals grown by additive-free synthesis are polydisperse in size, exhibit non-homogeneous shape or common polyhedral morphologies.

We have developed a new additive-free synthesis that results in the formation of monodispersed crystals with a large variability of morphologies, while keeping the crystallographic structure nearly identical. [2-5] The set of crystals generated include rare polyhedral shapes, hollow structures and paradoxical morphologies that are not classifiable according to conventional rules (Figure). Our work provides new fundamental insights in the growth of chiral crystals and aggregates, opening up opportunities for their use as 3D objects for nanotechnological applications.



[1] H. Furukawa et al. Science 341 (2013) 974
[2] M. C. di Gregorio et al. Nat. Commun. 11 (2020) 380
[3] M. C. di Gregorio et al. Nat. Commun. 12 (2021) 957
[4] M. C. di Gregorio et al. J. Am. Chem. Soc. 140 (2018) 9132
[5] H. Nasi et al. ChemRxiv DOI 10.33774/chemrxiv-2021-brq1h

OR028

Crossed beams and theoretical studies of the combustion relevant $O(^3P)$ + acrylonitrile reaction

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The environmental and human health effects of acrylonitrile, a volatile organic compound (VOC) with formula CH_2CHCN, are varied and diversified, as are the uses of this nitrile compound. As a matter of fact, CH_2CHCN is the main repetitive unit of acrylic and modacrylic fibers, and it is one of the constituents of many thermoplastics, such as ASA (acrylonitrile-styrene-acrylate) and ABS (acrylonitrile-butadiene-styrene). At the same time, acrylonitrile is a toxic air pollutant with possible carcinogenic effects and it can react with other VOCs to contribute to photochemical smog. So, an efficient treatment of the tail gas of acrylonitrile plant is essential to regulate its emission into the atmosphere, with thermal combustion and selective catalytic combustion being the most useful processes for this purpose. Within this framework, we have focused on the most important reaction occurring during the combustion of acrylonitrile, that is $O(^3P)$ + acrylonitrile, being atomic oxygen one of the main characters of combustion environments. It should be noted that the $O(^3P)$ + acrylonitrile reaction is also relevant during the combustion of other materials, such as coals and low-rank fossil fuels, because the thermal decomposition of pyridinic and pyrrolic species generates many nitrogen-bearing compounds, including acrylonitrile, whose further oxidation can result in nitrogen oxide (NO_x) byproducts. In this work, we have investigated the dynamics at the molecular level of the $O(^3P)$ + acrylonitrile reaction by exploiting the crossed molecular beam technique with mass spectrometric detection and product time-of-flight (TOF) analysis, coupled to synergistic theoretical calculations of triplet and singlet potential energy surfaces (PESs) and statistical (RRKM/Master Equation) estimates of product branching fractions (BFs), as successfully done in recent years for a variety of bimolecular reactions of relevance in combustion [1] as well as in astrochemistry.[2] This combined effort has permitted to elucidate the micro-mechanism of the $O(^3P)$ + acrylonitrile reaction, including the central role of the nonadiabatic phenomenon of intersystem crossing (ISC), and to characterize the primary products and their BFs. We have found that the reaction leads dominantly to the spin-forbidden CO + CH_2CNH (ketenimine) product channel (BF 0.9) *via* ISC from the triplet to the singlet PES, and to a minor extent (BF 0.1) to H + HCOCHCN adiabatically on the triplet PES. All these findings are expected to be useful to improve combustion models. Acknowledgments: This work was supported by Italian MUR and University of Perugia (Department of Excellence-2018-2022-Project AMIS) and by MUR (PRIN 2017, MAGIC DUST, Prot. 2017PJ5XXX). P.L. acknowledges support from the Marie Skłodowska-Curie project "Astro-Chemical Origins" (Grant No. 811312). D.M. thanks ASI (DC-VUM-2017-034, Grant No. 2019-3 U.O Life in Space).

[1] G. Vanuzzo et al. J. Phys. Chem. A 125 (2021) 8434

[2] L. Mancini et al. J. Phys. Chem. A 125 (2021) 8846

OR029

New clay-based geopolymers filled with halloysite stabilized microparticles and beeswax

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In the last few years, interest in developing new eco-friendly and low-cost materials that offer new perspectives in environmental remediation technologies is growing. For instance, geopolymeric materials are inorganic polymeric materials with an amorphous network of aluminosilicates that can be synthesized from industrial by-products or natural clays. As a matter of fact, nanoclays are widely employed to develop modern multifunctional products due to their peculiar physicochemical properties. Among them, halloysite nanotubes (HNTs) are emerging natural aluminosilicates with a singular hollow tubular structure, eco-compatibility, non-toxicity and low cost[1] and can be employed as aluminosilicate precursors in the geopolymerization process. In this work, we propose the preparation and characterization of new hybrid halloysite-based geopolymers filled with microwax particles obtained from dried Pickering emulsion[2] and with beeswax for comparison. Notably, wax microparticles were successfully embedded in the geopolymeric matrix, achieving a uniform inclusion of wax into the structure, as confirmed by SEM analysis. The structure and properties of these materials were investigated with FTIR, XRD and TGA. The filling of geopolymers with both wax and microwax induced significant changes in the wettability properties obtaining the hydrophobization of the surface. Beeswax was subsequently used as sacrificial material and it was removed from the geopolymeric matrix modifying the porosity of the pristine materials and increasing the water vapor permeability in these samples.

The final filled products represent the starting point for the design of new hybrid and green geopolymers including a phase change material with a high thermal capacity and that can act as an energy storage material.

[1] M. M. Calvino et al. Colloids Surf. A Physicochem. Eng. Asp. 641 (2022) 128530
[2] L. Lisuzzo et al. Adv. Mater. Interfaces (2022) 2102346

OR030

The effect of point defects on TiNiSn and ZrNiSn thermoelectric properties

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In recent years, thermoelectric (TE) materials have become of increasing interest, thanks to their electronic and transport properties which make them very suitable as green energy sources. Among different TE materials, the half-Heusler (HH) alloys are of particular interest for their excellent electronic transport properties and their tunable band gap, which allow the possibility of tailoring TE efficiency.[1] A literature survey shows that different samples of nominally stoichiometric HH compounds have extremely scattered values of electrical conductivity and Seebeck coefficient. Such a dispersion of data can be ascribed to residual secondary phases and point defects that affect the charge carrier concentration.

In this study, we present a combined experimental and theoretical approach aimed at investigating the role of point defects on the electronic and thermoelectric properties of TiNiSn and ZrNiSn alloys. Calculations were performed with CRYSTAL[2], an ab-initio quantum mechanical code, in which the Boltzmann transport equation within the rigid-band approximation was recently implemented[3] and exploited.[4] Experimental investigations confirmed that interstitial Ni defects in TiNiSn increases the metallic behaviour of the defective structure with respect to the defect free structure, raising the electrical conductivity and lowering the absolute values of the Seebeck coefficient. DFT modelling validates this result and paves the way for the synthesis of the ZrNiSn alloy for which calculations suggest that, contrary to the case of TiNiSn, (i) interstitial and anti-structure nickel defects decrease the conductivity and that (ii) Sb-doping increases the power factor, as shown in Figure 1.

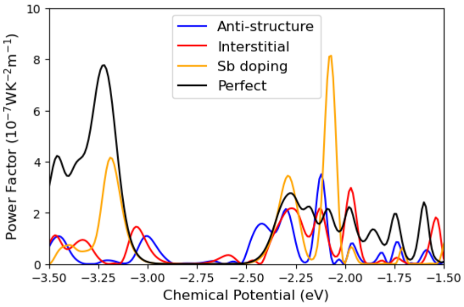

Figure 1. Computed power factor at 300 K as a function of chemical potential. Black line for the perfect ZrNiSn, yellow line for the Sb doped structure, red line for the structure containing one interstitial Ni, blue line for the structure containing the anti-structure defect.

[1] X. Shi et al., Int. Mater. Rev., 61, 379-415, 2016
[2] R. Dovesi et al., WIREs Comput. Mol. Sci., 8, e1360, 2018
[3] G. Sansone et al., J. Chem. Phys., 147, 114101, 2017
[4] A. Dasmahapatra et al., J. Phys. Chem. C, 124, 14997-15006, 2020

OR031

Topology of the Electron Density and its Laplacian from Periodic LCAO Calculation on f-Electron Material

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The nature of the chemical bonding (CB) of f-electrons is as fascinating as still puzzling. Many aspects of this intricate phenomenon are widely studied since its full rationalization would have both fundamental and technological relevance. The main objective of our research work is the development of new methodologies for a better description of CB features for materials containing Lanthanides and Actinides. The most rigorous technique allowing for a description of multiple aspects of CB is Bader's quantum theory of atoms in molecules and crystals (QTAIMAC). At the core of this methodology is the topology of the electron density, and therefore, it can in principle be adopted both experimentally and theoretically, thus allowing for a mutual validation of the two approaches. In this context, we have extended the TOPOND library of the CRYSTAL code[1], which implements the QTAIMAC, to f- and g- type basis function. Then, we applied our new methodologies to systems that have already been experimentally studied in order to validate our approach. In particular, we studied the papers by Gianopoulos et al.[2] and by Zhurov et al.[3], which studied, from an experimental point of view, uranium-containing compounds, respectively the $[PPh_4][UF_6]$ and the $Cs_2UO_2Cl_4$ crystals. On our side, we studied these systems from the theoretical point of view and we got a really coherent description of many aspects of the chemical bond with experimental data[4,5]. Since a remarkable agreement represents a strong mutual validation of both approaches, we decided to study a common system, the UCl_4, along with the Toledo university and to try to understand if a union of the experimental and theoretical methodology could give us a further improvement.

[1] Dovesi R. et al., Quantum-mechanical condensed matter simulations with CRYSTAL, Wiley Interdisciplinary Reviews: Computational Molecular Science 8.4 2018, e1360
[2] Gianopoulos C.G., Zhurov V.V., Pinkerton A.A., Charge densities in actinide compounds: Strategies for data reduction and model building, IUCrJ 2019, 6, 895–908.
[3] Zhurov V.V., Zhurova E.A., Pinkerton A.A., Chemical Bonding in Cesium Uranyl Chloride Based on the Experimental Electron Density Distribution, Inorg. Chem. 2011, 50, 6330–6333.
[4] Cossard A., Desmarais JK., Casassa S., Gatti C., Erba A., Charge Density Analysis of Actinide Compounds from the Quantum Theory of Atoms in Molecules and Crystals, The journal of physical chemistry letters 2021, 12 (7), 1862-1868.
[5] Cossard A., Desmarais JK., Casassa S., Gatti C., Erba A., Topology of the Electron Density and of Its Laplacian from Periodic LCAO Calculations on f-Electron Materials: The Case of Cesium Uranyl Chloride, Molecules 2021, 26 (14), 4227.

OR032

Towards *in situ* multinuclear MAS NMR mapping of chemical reactions

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A recently developed time-resolved *in situ* multinuclear solid-state NMR spectroscopic approach has the ability to detect transient species and fingerprint the critical and rapid mineralogical changes on a time scale of seconds.[1] Magic angle spinning (MAS) NMR spectroscopy is a distinctive tool for the investigation of hydration kinetics due to its unparalleled ability to probe molecular level transformations and to equally detect and quantify crystalline, amorphous and surface species. We have employed the fast analysis capabilities of this innovative technique to investigate the early hydration behaviour of cement phases that revealed the hydrated dissolved species, metastable as well as the stable precipitated solid phases, concurrently. *In situ* ^{1}H MAS NMR spectroscopy fingerprinted all the hydrated proton bearing phases while ^{27}Al MAS NMR easily distinguished the anhydrous and hydrated aluminate phases. In addition, if other NMR-friendly nuclei such as ^{23}Na or ^{29}Si are present in the sample, huge amount of complementary molecular-level information can also be gathered by this MAS NMR spectroscopic technique and can also be applied to other avenues of material science.

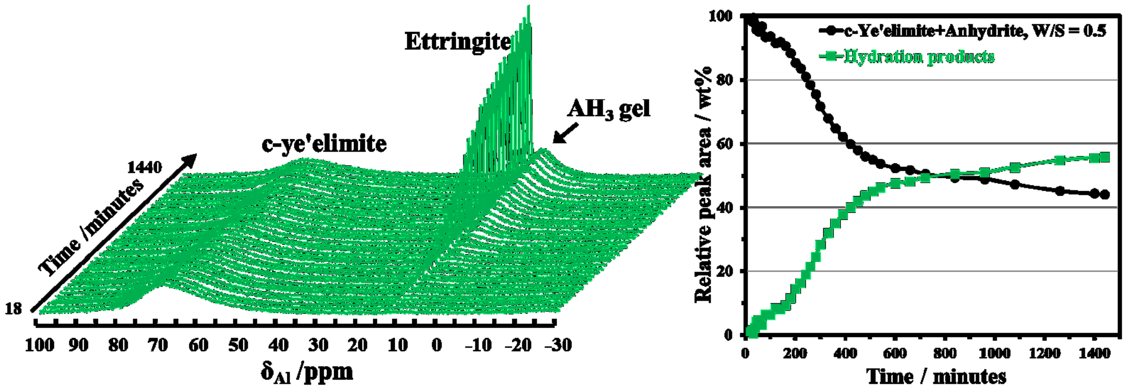

Figure 1. Stacked plot of time-resolved *in situ* ^{27}Al MAS NMR spectra and the time dependence of the peak areas due to reactant (ye'elimite) and hydration products (sum of ettringite, monosulfate, and aluminum hydroxide gel) derived from the time-resolved *in situ* ^{27}Al MAS NMR spectra.

[1] G. Paul et al. J. Phys. Chem. C 125 (2021) 9261.

OR033

Condensed Supramolecular Helices: The Twisted Sisters of DNA

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Folding and condensation of chiral macromolecules on the nano- and micro-scale play fundamental roles in living organisms. Condensation of DNA helices into hexagonally packed bundles and toroids represents an intriguing example of this functional organization, which allows DNA to fulfil fundamental biological functions and to fit into compartments like cells and virus capsids [1,2]. The condensation models are based on the unique polyelectrolyte features of DNA, however here we could reproduce a DNA-like condensation with supramolecular helices of small chiral molecules, thereby demonstrating that it is a more general phenomenon. We show that the bile salt sodium deoxycholate can form supramolecular helices upon interaction with oppositely charged polyelectrolytes of homopolymer or block copolymers. At higher order, a controlled hexagonal packing of the helices into DNA-like bundles and toroids could be accomplished (Figure 1). The results disclose unknown similarities between covalent and supramolecular non-covalent helical polyelectrolytes. They are relevant to gain deep understanding of supramolecular self-assembly fundaments and to inspire innovative research lines, up to visionary ideas of constructing supramolecular versions of biological macromolecules [3].

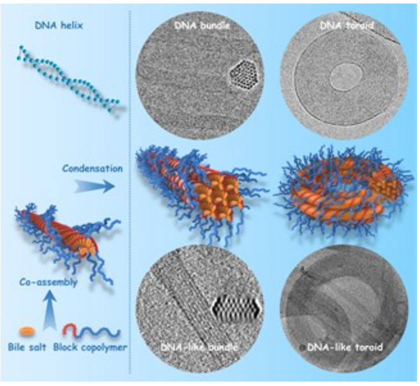

Figure 1

[1] S. M. Douglas et al. Nature 459 (2009) 414–418.
[2] M. E. Cerritelli et al. Cell 91 (1997) 271–280
[3] G. Du et al. Angew. Chem. Int. Ed. 61 (2022) e202113279

OR034

Ions mobility studies in polymer electrolytes for advanced lithium batteries by multinuclear NMR spectroscopy

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Li-ion batteries (LiBs) have currently taken over the market of high-tech personal devices and are aggressively advancing toward the evolution of sustainable transport and grid storage. Along with the need to improve batteries in terms of cost, energy density, charge time and cycle life, an important objective is battery safety, which is difficult to achieve without compromising electrochemical performance. To address these issues, solid polymer electrolytes (SPEs) have been developed, but they exhibit poor ionic conductivity at room temperature and weak interfacial compatibility with electrodes. On the contrary, gel polymer electrolytes (GPEs), obtained by trapping a large amount of liquid electrolytes in a polymer matrix, manage to provide solid-liquid two-phase conduction and good interfacial contact with the electrodes.[1] On the other hand, the introduction of a polymeric matrix into the electrolyte prevents liquid electrolyte from leakage and also improves safety of the device by reducing flammability and suppressing the formation of lithium dendrites. Another very promising approach to improving the intrinsic safety of batteries is to use ionic liquids (ILs) as an electrolyte component. [2]

More recently, a new concept for polymer electrolytes has been proposed based on a single lithium-ion (Li-ion) conducting-SPEs, which have anions covalently bonded to the polymer, inorganic backbone, or immobilized by anion acceptors.[3] For this purpose, polymer electrolytes based on ionomers such as Nafion, with perfluorinated ionizable groups (−CF2SO3−), are interesting due to the presence of weak coordinating anions, providing a high concentration of counter ions in nonaqueous media, which in turn favors the ion transport.[4]

Multinuclear magnetic resonance (NMR) spectroscopy has been successfully and productively applied to investigate the transport properties in PEs. It is a powerful method to probe ion and polymer dynamical process over a span of some ten orders of magnitude (in time or frequency) from spin-lattice relaxation (T_1) to pulsed field gradient diffusion (PFG-SE). The relevant nuclei include ^{7}Li and ^{19}F, for probing the environments and mobility of the ions, and ^{1}H and ^{13}C for the polymer. Recently, with renewed interest in sodium batteries, ^{23}Na is returning to the scene as well. [5] The most important and recent experimental results obtained in the author's laboratory on the investigation of different polymer electrolytes by nuclear magnetic resonance (NMR) spectroscopy will be presented and discussed. Various examples will show the ability of NMR to probe cation-anion interactions or successfully estimate the ion transport number or issues directly related to ion mobility and ion-polymer interactions in PEs, both for lithium and sodium batteries.

This work is supported by the M-ERA.NET and POR-Calabria FERS-FSE 2014-2020 through the INNENERMAT project.

[1] Yong An et al.. Small 18 (2022) 2103617.
[2] R. Poiana,…I. Nicotera…et al., Electrochimica Acta 401 (2022) 139470.
[3] H. Zhang et al., Chem. Soc. Rev. 46 (2017) 797–815.
[4] I. Nicotera, et al., J. Phys. Chem. C 123 (2019) 27406−27416.
[5] C. Simari, …I. Nicotera, Electrochimica Acta 410 (2022) 139936.

OR035

Designed Metallic Ceramic Based Catalysts for Biomass Valorisation

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The continuous population growth and technological development inevitably led to high energy demand, which can no longer be sustained by fossil fuels without deeply damaging our environment. Among renewable energy processes, a promising one is *biomass valorisation* to produce *(bio)fuels* from waste. Despite biofuels hold the same potential of fossil fuels, their production is still neither practical nor economically feasible. One of the limiting factor is the lack of sustainable catalysts. In fact, in this context, even noble metals are unsuitable, due to the high costs and susceptibility to be poisoned under the reaction conditions. In this respect, metallic ceramics (MCs) are a promising alternative, thanks to their good catalytic activity alongside high chemical stability, and tuneable selectivity. In our group, we focus on the design of tailored MCs based catalysts, prepared via a greener sol–gel based process (called the *urea-glass-route*), which leads to crystalline and well-defined, in composition and size, nanoparticles with high surface area.

The catalytic activity of Ni_3N@C, Fe_3C, $Fe_{2.7}Mn_{0.3}C$, among others, was investigated in biomass related model reactions, such as hydroconversion of levulinic acid (toward N-substituted pyrrolidones), oxidation of isoeugenol and vanillyl alcohol (to vanillin), and furfural conversion (into furan and furfuryl alcohol) [1-3]. The catalysts were tested as prepared, with no need for post-synthesis purification, activation, or co-catalysts addition, and their characterization after testing, demonstrated their stability under the reaction conditions. The catalytic studies showed that the activity of tested MCs was superior to those of the parental metals, with the further advantage to allow tuning selectivity. For instance, in the levulinic acid hydroconversion [1], Ni^0 always led to the main product (1-ethyl-5-methylpyrrolidin-2-one), regardless of the conditions, while Ni_3N favoured the formation of the secondary product (1-ethyl-5-methyl-1,3-dihydro-2H-pyrrol-2-one) for longer reaction time, leading to the main product only at shorter reaction time. For the vanillin production [2], although the catalytic activity of the ternary system, $Fe_{2.7}Mn_{0.3}C$, was similar to that of Fe_3C, the incorporation of a second metal had an effect on material stability and selectivity, suggesting that ternary systems might allow controllable oxidation reactions. Finally, in the furfural conversion [3], the Ni_3N catalyst allowed tuning the selectivity toward furan or furfuryl alcohol (decarbonylation and hydrogenation products, respectively) by varying reaction temperature, while maintaining a furfural conversion above 80%, in each case.

[1] C. Defilippi, D. Rodriguez-Padron, R. Luque, C. Giordano, Green Chemistry, Green Chem. 22 (2020) 2929
[2] C. Defilippi, D. Rodríguez-Padrón, R. Luque, L. Winchester, C. Giordano, J. Clean. Prod. 347 (2022)
[3] C. Jiménez-Gómez, C. Defilippi, J.A. Cecilia, R. Moreno-Tosta, P. Maireles-Torres, C. Giordano, Molecular Catalysis 487 (2020) 110889

OR036

A further step towards μ-SOFCs: high pressure structural characterization of doped ceria electrolytes

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In the last decades the growing need to produce energy in a sustainable way has led to an increased interest towards Solid Oxide Fuel Cells (SOFCs), devices that combine high efficiency and considerably low pollutants emissions. In the present framework, the possibility of obtaining fuel cells of reduced dimensions (μ-SOFCs) that are portable power sources for laptops, small medical or industrial devices and so on is highly desirable [1].

To date, our research group is evaluating the possible use of doped ceria electrolytes in μ-SOFCs. In fact, when a small fraction of trivalent rare earth ions (RE) is inserted into the fluorite-like (F) structure of pure ceria, the occurrence of not associated oxygen vacancies that are free to move through the lattice is observed, and the $Ce_{1-x}RE_xO_{2-x/2}$ systems become good conductors of O^{2-} ions in the intermediate temperature range (673 – 973 K). However, when the RE amount increases, the F structure can no longer incorporate the doping ions, and different structures characterized by a lower ionic conductivity appear [2].

In μ-SOFCs, due to the reduced dimensions, the electrolyte is deposited as a thin film on a proper substrate, thus experiencing a tensile strain, due to the oxide-substrate lattice mismatch, which promotes the passage of O^{2-} ions through the F lattice, thus increasing the ionic conductivity of the system. However, if the strain is too high, it is released with the formation of dislocations, that reduce the oxygen ions mobility. Since a more compressible electrolyte should be able to better tolerate strain without creating dislocations, our research group undertook a high-pressure x-ray diffraction study on different RE-doped ceria systems (RE= Lu, Sm, Nd/Tm and Gd/Sm) to evaluate their compressibility, and thus the most suitable doped ceria electrolytes to be used in μ-SOFCs [3]. Starting from the present experiments, our group also developed a novel approach to evaluate the amount and composition of the C phase defects, clusters having the typical RE_2O_3 cubic structure that are responsible for the drop in the ionic conductivity of these systems, which is generally observed at quite low dopant amount [4]. A full overview of the performed high pressure structural studies will be presented.

[1] A. Evans et al. J. Power Sources 194 (2009) 119
[2] C. Artini Inorg. Chem., 57 (21) (2018) 13047
[3] S. Massardo et al. Coatings 11 (2021) 724
[4] C. Artini et al. Inorg. Chem., 60 (2021) 7306

OR037

Biophysico-chemical studies of G-quadruplexes: from oncogene promoters to aptamers

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First found in telomeric DNA, higher-order DNA structures called G-quadruplexes (G4s) draw great attention as potential drug targets [1]. G4s are formed by guanine-rich sequences that build-up into guanine tetrads stabilized by Hoogsteen hydrogen bonds and monovalent cations [2]. Beyond telomere, G4s have been also located in other functional genomic regions i.e., oncogene promoters, opening for the chance to modulate transcription with minimal adverse side effects as they in principle allow for high drug selectivity [3]. Indeed, G4s in oncogene promoters have been considered as novel potential targets for anticancer therapy relying on the idea that the overexpression of oncogenes containing G4 structures can be downregulated by G4-binding ligands *in vivo* [4]. Another very attractive tool in both therapeutic and diagnostic applications are aptamers based on the G4 motif. Aptamers are single-stranded oligonucleotides that, thanks to their distinctive three-dimensional shape, can bind with high affinity to specific targets and, in most cases, modulate their biological functions [5]. However, the design of new aptamers is difficult because many factors affecting their activity and stability have not yet been elucidated.

The knowledge of the energetics of G4 formation is a crucial point in view of their potential therapeutic use both as targets and as therapeutic agents. Here, in line with our previous studies [6,7], we investigated the energetic aspects of both G4 assembly and G4-ligand interactions to deepen their physico-chemical features.

[1] Hurley L. H. et al. Pharmacol. Ther. 85 (2000) 141–158
[2] Bochman M.L. et al. Nat. Rev. Genet. 13 (2012) 770–780
[3] Balasubramanian S.et al. Nat. Rev. Drug Discov. 10 (2011) 261–275
[4] Shi D.F. et al. J Med Chem. 44 (2001) 4509-4523
[5] Keefe A.D.et al. Nat Rev Drug Discov 9 (2010) 537–550
[6] Pagano B. et al. Biophys. J. 94 (2008) 562-569
[7] Amato J. et al. Nucleic Acid Ther. 30 (2020) 414-421

OR038

Liposome@PDA microspheres for fast and highly efficient removal of methylene blue from wastewater

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An environmentally friendly and high-efficiency material for wastewater remediation was developed usefully exploiting mussel-inspired chemistry. Hollow micro-spheres based on polydopamine (PDA) were obtained by coating phospholipid liposomes with this naturally inspired polymer [1]. Prepared Liposome@PDA microspheres were used for the first time as an adsorbent material for the removal of methylene blue (MB), a cationic dye widely used in textile and paper industries, from aqueous solutions. Liposomes were prepared through the extrusion method using membranes with a porosity of 200 nm. Then, vesicles were coated with PDA by inducing the self-polymerization of the dopamine into the liposome suspension. Liposome@PDA microspheres were fully characterized by DLS, Zeta potential analysis, TEM microscopy, and FTIR spectroscopy. Then, the capability of our systems to remove MB from the water was evaluated in terms of adsorption capacity (qt) by changing the process parameters. It is known that the adsorption process involves mainly electrostatic and π-π stacking interactions, so it was first investigated the effect of the pH on the process. Then effects, temperature, MB concentration, amount of Liposome@PDA, and contact time on the adsorption process were also investigated. Results showed that the highest qt was obtained in weakly alkaline conditions (pH = 8.0), where the electrostatic interactions between the compounds are maximized, and that it could reach up to 395.4 mg g^{-1} at 298 K. Removal efficiency was high, up to 96% and with a very high adsorption rate. Results show that the data well fit a pseudo-second order kinetic model and the Langmuir isotherm model. Moreover, the process seems to be spontaneous and endothermic in the realized experimental conditions (ΔG^0 = -12.55 kJ mol^{-1}, ΔH^0 = 13.37 kJ mol^{-1}) in the investigated experimental conditions. The applicability of Liposome@PDA microspheres to tap water, NaCl 0.1 M and model wastewater was demonstrated. Finally, the regeneration of the Liposome@PDA microspheres after the adsorption process was carried out using methanol. Results showed excellent reusability performances after three cycles.

[1] V. De Leo et al. Int. J. Mol. Sci. 22 (2021) 11916

OR039

Amphiphilic coating induces a hierarchical organization in cerium oxide nanoparticles

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Recently, the controlled clustering of nanoparticles (NPs) building blocks into defined geometric arrangements opens a new research area in soft-materials with original physico-chemical properties. NP ordered clusters not only allow the combination of individual NP properties but also takes advantage of the interaction between neighboring NPs [1]. Here, a button-up approach let to clusters of coated cerium oxide nanoparticles (CeO_2-NPs) dispersed in water [2]. The hydrophobic interactions between chains of the organic coating cause the formation and the coexistence of ordered structures, such as FCC or pseudo-hexagonal phases [3]. These structures are discussed in terms of geometrical parameters including NPs diameter, distance between neighboring NPs, and ligand length. In particular, the length of the amphiphilic molecules in the coating layer of the NPs have a crucial effect in ruling the ordering phases, and so the final physico-chemical parameters of ordered structures. To understand how the order in the structure can affect the properties of NPs, PL measurements have been performed. Form which the different structured organization of NPs and probably the relative amount between them leads to different fluorescence intensity.

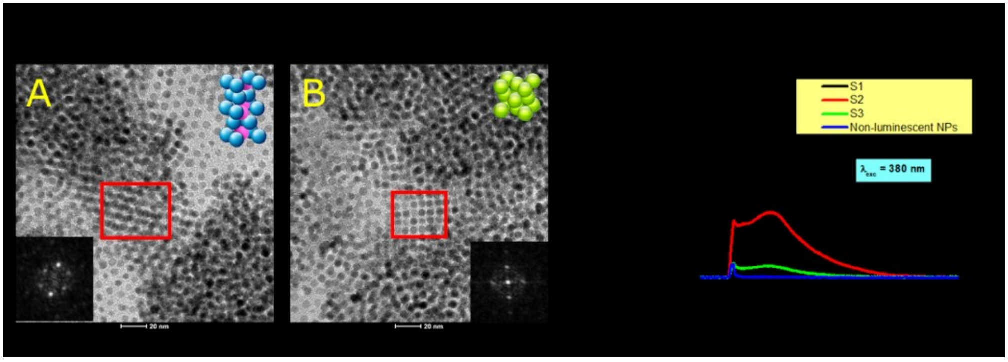

Figure1. TEM images and FTT of pseudo-hexagonal phase **(A)**, FCC phase **(B)** of coated CeO_2-NPs, and PL spectra of three different samples with different amounts of ordered structures.

[1] Z. Lu et al. Chem. Soc. Rev. 41 (2012) 6874
[2] N. Gallucci et al. Nanomaterials 11 (2021) 542
[3] B. Pansu et al. Soft Matter 17 (2021) 6461

OR040

Dynamic fluctuations of nonlinear optical response of organic molecules

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The design of organic compounds with commutable second-order nonlinear optical (NLO) response have motivated a number recent works, owing to their potential exploitation in sensors or as active components in optoelectronic and photonic devices, such as logic gates or high-density optical memories. In all these applications, a key figure of merit of the switch is the contrast in the first hyperpolarizability between the different forms generated through controlled chemical conversions. In the quest of better and tunable NLO organic materials, quantum chemical calculations proved highly helpful in gaining fundamental insights on the various factors governing the magnitude and character of molecular first hyperpolarizabilities [1], be they intrinsic to the molecular structure and arising from symmetry, chemical substitution or π-electron delocalization, or induced by the laser probe or by external contributions such as frequency dispersion and environment effects. However, most theoretical reports assume a rigid picture of the investigated systems, with hyperpolarizabilities being computed solely at the gas phase equilibrium geometry of the chromophores. Yet, our recent theoretical reports combining classical molecular dynamics (MD) simulations and DFT calculations have evidenced a significant role of geometrical fluctuations, which may induce broad distributions of NLO responses, and even generate them in some cases [2].
This presentation will showcase the results of a few of these studies in which this multiscale approach has highlighted the crucial role of dynamical disorder onto the NLO responses. Selected examples will include ionic complexes in the liquid phase, emphasizing the effects of explicit solvation, concentration and chromophore aggregation, but also lower dimensionality solid systems such as self-assembled monolayers (SAMs) based on indolino-oxazolidine [3] or azobenzene [4] switches, and finally nanoparticles formed by donor-acceptor chromophores in water [5].

[1] C. Tonnelé et al. Phys. Chem. Chem. Phys 20 (2018) 27658
[2] K. Pielak et al. J. Phys. Chem. C 122 (2018) 26160
[3] C. Tonnelé et al. Phys. Chem. Chem. Phys. 20 (2018) 21590
[4] C. Tonnelé et al. Chem. Mater. 31 (2019) 6759
[5] L. Lescos et al. Phys. Chem. Chem. Phys. 23 (2021) 23643

OR041

On MMA-DMAEMA copolymerization catalyzed by Cu(I) complexes: presentation abstract

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Atom Transfer Radical Polymerization (ATRP) is a versatile polymerization technique. However, the catalytic mechanism is yet to be determined. To investigate this mechanism the copolymerization of methylmethacrilate (MMA) or dimethylaminoethylmethacrilate (DMAEMA) was performed varying the monomer feed composition, which means increasing MMA fraction while decreasing DMAEMA one, while maintaining constant the total number of moles. A greater reactivity for DMAEMA was observed, thus suggesting a fundamental role of the Cu catalyst, since the aminic group of DMAEMA is a good coordinating group towards Cu(I). As already pointed out by Matyjaszewski et al. [1] the equilibrium constant K_{ATRP} varies depending on the ligands employed to form the catalytic complex. DFT calculations for Me_6Tren, BPY, N-(2-pyridylmethylene)methylamine and Me_4Cyclam evidenced the formation of an ion couple in the catalytic complex, which means the coexistence of $[\text{Ligand-Cu}]^+$ and $[CuBr_2]^-$ in solution. The ion couple is also present when DMAEMA coordinates to the complex, and it could play a crucial role in determining catalysis mechanism. DMAEMA-MMA copolymerization experiments were performed employing BPY and Me_6Tren decreasing the DMAEMA/MMA ratio in feed, and in both cases DMAEMA fraction in the polymer exceeds the fraction in reaction feed. This means DMAEMA is inserted in the polymer chain more rapidly with respect to MMA. This should be due to a more favored coordination of DMAEMA to the anionic copper atom, which leads to increased local concentrations of that monomer in the reaction batch. NMR and CV observations on the catalysts pointed out that complex formation and DMAEMA coordination lead to variations of both chemical shifts and $E_{1/2}$, sign that monomer coordination impacts properties of the system. Indeed, from both experimental and computational ^{1}H-NMR data a shift towards highest chemical shifts is observed upon coordination of DMAEMA. This was expected since Cu drains electron density from DMAEMA de-shielding its protons.

[1] W. Tang et al. J. Am. Chem. Soc. 130 (2008) 10702

OR042

A new hyphenated technique combining FTIR Spectroscopy and Barometry to study mass transport of pure and mixed gases in polymers

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The solubility of multiple gases in polymers is usually measured with gas chromatography (GC) by investigating *ex situ* the concentration of each species in the gas phase at sorption equilibrium [1].
In this work, a new hyphenated technique is developed to characterize *in situ* the solubility and sorption kinetics of pure and mixed gases in polymers. FTIR Spectroscopy in the transmission mode is coupled with Barometry to calibrate the IR signals of the low MM species in the gas and the polymer phases. The case of carbon dioxide and methane in rubbery polydimethylsiloxane (PDMS) is investigated at ambient temperature and up to 9 bar [2]. Specifically, two separate IR approaches are followed and validated by comparison with literature data on the same polymer – penetrants system [1]. First, samples of the pure gases are prepared at fixed pressure and temperature and their IR absorbance spectra are measured. The IR signals are calibrated with density data from the NIST REFPROP 7 database. These calibration curves allow to measure spectroscopically the concentration depression during sorption experiments of pure CO_2 or CH_4 in PDMS. The method performances are directly compared with the simultaneous pressure decay technique. In the case of the CO_2 – CH_4 gas mixture, the gas phase IR signals of CO_2 are successfully used to measure its concentration in PDMS. A second spectroscopic approach consists in allowing the IR beam to pass through the polymer film with the aim to measure the IR spectrum of the penetrant as well. The IR peak centered at 4954 cm^{-1} which identifies the CO_2 absorbed in the polymer is calibrated with sorption experiments of pure CO_2 in PDMS [3]. Its molar absorptivity is then used to quantify spectroscopically the CO_2 concentration in the polymer when it is in contact with a binary gas mixture of the two components. Since the polymer spectrum is measured as well, this second approach generally allows to quantify polymer swelling and to identify host-guest interactions [3]. The composition of the gas phase at sorption equilibrium is always evaluated from the IR signals of the gas phase.
Being both methods applied *in situ*, sorption kinetics are easily measured. Also, no thermodynamic models are needed to treat the gas mixture at sorption equilibrium since its composition is retrieved from the IR spectrum itself. The hyphenated technique is limited to heteronuclear penetrants. The apparatus used in this work has been tested for a maximum operating pressure of the gas mixture equal to 9 bar and is being extended to glassy polymer as well.

[1] G. Genduso et al. J. Mem. Sci. 577 (2019) 195–204
[2] V. Loianno et al. J. Mem. Sci. 652 (2022) 120445
[3] V. Loianno et al. Ind.&Eng. Chem. Res. 60 (2021) 5494−5503

OR043

Fe,Ni-Based Skutterudites PLD Thin Films and On-Chip Device

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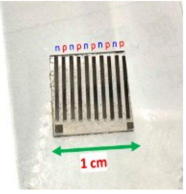
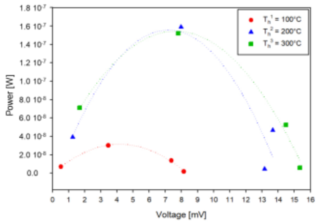
After a deep study of thermoelectric properties of Fe,Ni-based skutterudite thin films, a further step towards a possible future application led us to the investigation of an on-chip thermoelectric thin film module composed of five pairs of *n*-type and *p*-type skutterudite legs. Thin film legs were prepared by pulsed laser deposition (PLD) using a Nd:YAG (266 nm, 10 Hz) laser at room temperature. The substrate (silica, 1 cm^2) was covered with a custom-made Nickel mask in order to selectively deposit the desired set of legs depending on the used target; then, it was manually shifted to deposit the other five legs composing the module, which appearance at this step is shown in fig. 1.



With the aim to improve the thermoelectric properties, the device underwent then to an annealing process in flowing Ar at 200°C for 3 h (following our previous study [1]) before depositing the Au contacts with a gold sputter. Ni wires were attached by means of a silver epoxy at the two ends of the device. The performance of the module was measured using ad custom-made apparatus, following the procedure previously reported by Saini et al. [2]. The generation of thermoelectric voltage was checked by manually heating up one side of the module by means of a hot plate (T_h up to 300°C) and cooling down the other side using a beaker full of ice. Temperatures were monitored while through two *K*-type thermocouples, while voltage (ΔV) was measure at the two ends of the device throw a voltmeter. This thermoelectric ΔV is acquired by using a variable resistance (in the range of 10 Ω to 10^6 Ω), called load resistance R_L, set in parallel to the module, and power was estimated at different temperatures (T_h = 100, 200 and 300°C) for each value of external resistance. Power results are displayed in fig. 2 as a function of the measured voltage. The peak value of the polynomial bell-shape fitting the experimental points is considered as the maximum power output of the device, which in this case is ≈ 0.16 µW, 3 to 4 magnitude orders bigger than what previously measured for oxide thin films by S. Saini et al. [2].



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[1] G. Latronico et al., in preparation
[2] S. Saini et al., Energy Convers. Manag. 114 (2016) 251-257.

OR044

Magnesium phosphate-based bone cements: physico-chemical study and colloidal approaches to tailor their properties towards orthopedic applications

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Magnesium phosphate-based cements (MPCs) have recently attracted great attention as materials for bone repair, because they possess some characteristics (faster setting, higher early strength, good biocompatibility and superior degradation behavior) that represent a valuable improvement with respect to Calcium Phosphate cements. In addition, *in vitro* studies suggest that Mg^{2+} ions stimulate osteoblast differentiation and inhibit osteoclast formation. [1] This contribution focuses on the most recent results obtained from our group in the investigation of the physico-chemical characteristics of MPCs and in the optimization of some of their features. A thorough investigation on the effect of the preparation conditions on the composition and on the main physico-chemical and mechanical properties will be first presented [2]. Then, this contribution will show that MPCs can be successfully formulated to release active molecules directly on the site of application: in particular, the results of the preparation and characterization of MPCs containing citrate will be presented. The choice of citrate relies on the evidence that it is an ion naturally present in bone, whose supplementation in the proximity of newly forming bone tissue has shown beneficial effects. The release of citrate upon incubation in aqueous media was studied, and we demonstrated that this molecule could be successfully released from the cements, while contributing to the alkalinization of the surroundings. The cytotoxicity of the materials toward human fibroblasts was also tested, revealing the importance of a fine modulation of released citrate to guarantee the biocompatibility of the material. [3] As a last example, this contribution will present an innovative strategy to prepare macroporous MPC cements. In fact, despite the great number of appealing features of MPCs, the lack of macroporosity, fundamental for cells permeation and bone ingrowth, is one of the main limitations hampering their full exploitation. To handle this issue, we used gelatin microparticles (prepared by a water-in-oil emulsion method) as templating agents for the creation of macroporosities. The simple incubation at physiological temperature of the MPCs-gelatin composites allows for gelatin dissolution and endows the inorganic matrix with hundreds-micron sized porosities. This dissolution step can also be used to release active molecules on site (in this case alendronate, a well-recognized drug for the treatment of osteoporosis). The kinetic study of the release phenomena has been studied in detail. [4] The final aim of this talk is to show that a Physico-Chemical and, in particular, a Colloidal Science approach enables to fully exploit the versatility and the potential of these materials, whose properties can be tailored according to specific requirements in the field of bone repair.

[1] Wu L, Feyerabend F, Schilling AF, et al *Acta Biomaterialia* 2015, *27,* 294–304.
[2] Gelli, R.; Mati, L.; Ridi, F.; Baglioni, P. *Materials Science and Engineering: C* 2019, *95*, 248–255.
[3] Gelli, R.; Di Pompo, G.; Graziani, G.; Avnet, S.; Baldini, N.; Baglioni, P.; Ridi, F. *ACS Biomater. Sci. Eng.* 2020, *6*, 5538–5548.
[4] Gelli, R.; Sforzi, L.; Montanari, F.; Ridi, F.; Baglioni, P. *Journal of Materials Science* 2022, *submitted.*

OR045

Unveiling Electrolyte Reactivity at Lithium Metal Anode with Density Functional Embedding Theory

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The metallic lithium (Li) represents the most promising anode material among the next generation of solid-state lithium batteries [1]. An efficient strategy to achieve durable and effective Li-anode batteries is by engineering the solid-electrolyte interphase (SEI) with purposely designed molecules. To this aim, the vinylene carbonate (VC) is one of the most used additives in conventional electrolytes. Some recent experiments proved that the VC promotes the formation of a stable and protective SEI layer between Li metal and electrolyte [2, 3]. Unless the well-known SEI composition, it is difficult to control the VC reactivity, that involves dissociation and polymerization at the electrode surface. Therefore, to dissect these tangled processes, here we present new atomistic insights on VC-Lithium SEI formation via first-principles calculations by Density Functional Embedding Theory (DFET) [4,5], see Fig. 1. Such approach has potentialities for modeling complex reactions at hybrid interfaces in electrocatalysis: it is well suited to combine the best feasible approaches for molecular species (in this case, hybrid HF-DFT for VC molecules and derivatives) and for Li metal electrode (semi-local GGA density functional).

Our results highlight different VC dissociation pathways, with formation of reactive radical species and localized cluster of Li_2O and Li_2CO_3. The use of hybrid-DFT-in-DFT embedding is crucial for obtaning energy barriers and qualtitative results in agreement with experiments [3]. Overall, the energetics and structural features of these intermediates improve the current understanding of SEI formation process and can be exploited to drive the reactions toward the desired interfacial properties.

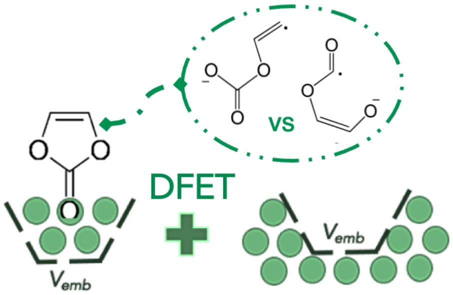

Figure 1. Sketch of the DFET approach to model reactivity at the lithium metal surface

[1] J. Janek, W. G. Zeier, *Nat Energy* 1 (2016) 16141.
[2] A. L. Michan et al. *Chem. Mater.* 28 (2016) 8149.
[3] Y. Kamikawa, K. Amezawa, K. Terada, *J. Phys. Chem. C* 124 (2020) 19937
[4] C. Huang, M. Pavone, E. A. Carter, *J. Chem. Phys*. 134 (2011) 154110
[5] C. Huang, A.B. Muñoz-García, M. Pavone, *J. Chem. Phys*. 145 (2016) 244103

OR046

Investigation of water/melamine interactions by combining core-level spectroscopies with theoretical calculations

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In the past few years, polymer or "soft" photocatalysts are emerging as a new class of materials for solar fuel production[1]. Among them, carbon nitride polymers (p-CNH) have been holding the stage since 2009, when *Wang et al.* have shown their ability to produce H_2 from water under visible light irradiation[2]. Despite their mesoscopic structure, recent theoretical investigations revealed that the water-splitting mechanism with p-CNH can be better explained as a photochemical reaction essentially confined on a single molecular unit[3].
With the perspective to perform *operando* electron spectroscopy studies, we exploited the chemical sensitivity of core-level spectroscopies (XPS, NEXAFS) to probe the local electronic structure of carbon nitride functional groups at the interface with water molecules. As model system, we used the melamine molecule, which is one of the p-CNH building blocks. The study was performed either at the solid state by realizing surface-supported water/catalyst complexes[4] and in solution by using the XPS µ liquid-jet technique[5]. For both systems, interpretation of the experimental data was supported by DFT-based calculations. Metadynamics studies were also performed to simulate liquid-jet experiments.

[1] T. Banerjee *et al.* Nat. Rev. Mater. 6 (2020) 268–190
[2] X. Wang *et al.*, Nat. Mater. 8 (2009) 76–80
[3] W. Domcke *et al.* ChemPhotoChem 3 (2019) 10–23
[4] V. Lanzilotto *et al.*, Nanoscale Adv. 3 (2021) 2359-2365
[5] M. Rosa *et al.*, *submitted*

OR047

Two faces of the same coin: coupling X-ray Absorption and NMR spectroscopies to investigate the exchange reactions between Cu and Zn coordination complexes

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Chemical reactions mainly occur in solution and the use of different techniques to monitor the advancement of a bimolecular chemical solution process is often a powerful tool for a satisfactory understanding of its underlying reaction mechanism [1]. Among the spectroscopic techniques that have been applied to follow chemical reactions occurring in solution, X-ray absorption spectroscopy (XAS) is a unique method that allows one to follow the variations in both the local electronic and structural configuration of a selected photoabsorbing atom [2]. For instance, recently XAS has been proven successful to identify the reaction mechanisms and intermediates of a series of processes involving non-heme iron complexes, where the metal center varies its oxidation state [2,3]. An advancement of this advanced experimental approach is to couple XAS with ^{1}H-NMR spectroscopy. Indeed, the two spectroscopic methods can be considered complementary when a chemical process occurring between metal complexes and organic molecules is taken into account. On the one hand, XAS allows one to quantitatively monitor the evolution of the oxidation state of a given metal ion and of its local structural environment with an unrivaled degree of accuracy. On the other hand, the fate of the organic components of the reaction, namely ligands and reagents, can be tracked by ^{1}H-NMR spectroscopy. Notably, a multivariate and theoretical analysis of the XAS data combined to the information attained by ^{1}H-NMR spectroscopy may provide deep insights into the chemistry of the given reactive system [1].

Herein, we combine X-Ray Absorption and ^{1}H-NMR spectroscopies with state-of-the-art Multivariate Curve Resolution and Density Functional Theory theoretical analyses to gain a comprehensive view on prototypical reactions involving the variation of the oxidation state and/or local structure environment of Cu and Zn metal ions coordinated by organic ligands. Specifically, we investigated: (i) the 2-cyano-2-phenylpropanoic acid reduction of the octahedral complex established by the Cu^{2+} ion with terpyridine to the tetrahedral complex formed by Cu^{+} and neocuproine; (ii) the dissipative translocation of the Zn^{2+} cation from hexaaza-18-crown-6 to two terpyridine moieties and back again to hexaaza-18-crown-6, employing as fuels the 2-cyano-2-phenylpropanoic acid and its para-chloro derivative.

Through our combined experimental and theoretical approach we gain insights into the nature, concentration time evolution and structures of all key metal (XAS measurements) and organic (^{1}H NMR measurements) species involved in the given reaction. We believe our method may prove to be useful in the toolbox necessary to reach a full mechanistic picture of reactive processes of interest in solution.

[1] D. Del Giudice et al. Chem. Eur. J. 28 (2022) e202103825
[2] G. Capocasa et al. J. Am. Chem. Soc. 141 (2019) 2299
[3] F. Tavani et al. Inorg. Chem. 59 (2020) 9979

OR048

Development of mesostructured acidic catalysts for the one-pot CO_2-to-DME process

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In the last two decades, dimethyl ether (DME) has received an increasing attention due to its potential in substituting diesel as fuel. Its industrial production is based on a two-step process in which methanol is first produced from syngas on Cu-based catalysts and subsequently dehydrated to DME over acidic catalysts. Starting from the progress made in syngas-to-DME conversion, the CO_2-to-DME process is taking place in the last decade, due to the possibility of revaluating CO_2, no longer as a waste, but as a valuable reagent. In this context, the one-pot dimethyl ether (DME) production from hydrogenation of CO_2 based on two-function (redox and acidic) catalysts is receiving increasing attention [1,2]. In this work, we propose different mesostructured acidic metal oxides as methanol dehydration catalysts to be used in physical mixture with a commercial Cu-based redox catalyst (CZA) for the CO_2-to-dimethyl ether (DME) one-pot production. Al-MCM-41, Al-SBA-15, TiO_2 and TiO_2-ZrO_2 mixed oxides, obtained *via* the sol-gel method, either in its conventional, solvothermal or EISA (Evaporation-Induced Self-Assembly) approach, were selected as mesostructured acidic systems. The ordered pore structure as well as the ideal pore size should render the active sites of the acidic catalyst easily accessible for CO_2 and H_2 and allow a homogeneous dispersion of the redox phase inside the mesopores, in view of the development of composite bifunctional catalysts. With the aim of understanding how the textural and acidic properties can be correlated with the performances and eventually design efficient dehydration catalysts, a careful study on the acidic sites was performed by both adsorption microcalorimetry with ammonia and FTIR-monitored adsorption of pyridine. The performances of the mesostructured dehydration catalysts, in form of physical mixtures with CZA, were compared with those of a commercial zeolite (ferrierite). The results highlighted a higher activity toward methanol dehydration for catalysts featured by Brønsted sites (ferrierite, Al-SBA-15 and Al-MCM-41); as of catalysts with Lewis sites only (TiO_2, $Ti_{0.77}Zr_{0.23}O_2$) better performances were shown in case of systems presenting sites of moderate strength ($Ti_{0.77}Zr_{0.23}O_2$). In the light of the above, Al-SBA-15 obtained through an EISA approach, demonstrated to be the most promising mesostructured dehydration catalyst in terms of selectivity to DME, despite being less active than ferrierite. Al-SBA-15 was subsequently used as support to obtain composite bifunctional catalysts by dispersing a $CuO/ZnO/ZrO_2$ redox phase inside the mesopores of the acidic phase. Two different functionalization methods were studied; the functionalization route that showed the best results is a wet-impregnation method modified with a self-combustion process.

[1] T.A. Semelsberger, R.L. Borup and H.L. Greene, J. Power Sources, 2006, 156, 497-511
[2] A. Alvarez, A. Bansode, A.Urakawa et al. Chem. Rev., 2017, 117, 9804-9838

OR049

Lacunarity as image descriptor for the evaluation of the dispersion degree of carbonaceous substrates in lubricants

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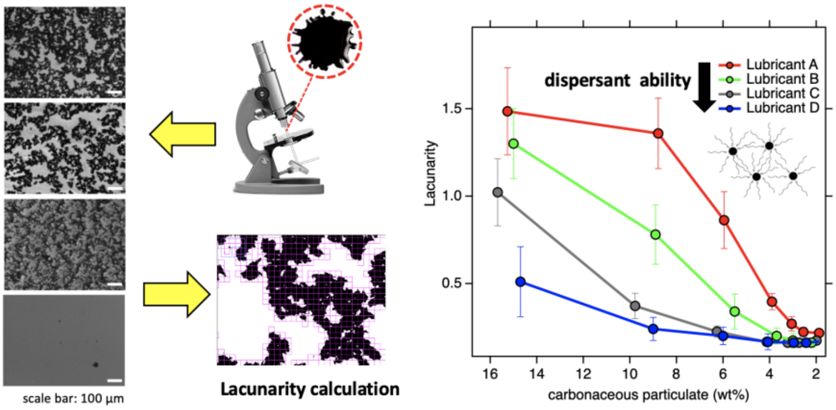
One of the main problems related to the aging of lubricants is the formation and accumulation of carbonaceous deposits inside the matrix. Consequently, the development of additives for the dispersion of these agglomerates is mandatory to increase the performances and life of the lubricant. Usually, the dispersant performances are evaluated by means of expensive and time-consuming engine tests. Here a new lab-scale method based on optical microscopy for the direct assessment of the dispersing capacity of a lubricant formulation is presented [1]. The degree of dispersion of the investigated samples is calculated directly on optical micrographs using the lacunarity descriptor which is defined as gappiness or heterogeneity associated to an image [2]. We demonstrate that low lacunarity values correspond to well dispersed systems while the presence of aggregates is responsible for an increase of micrograph lacunarity. The method was validated on reference oils and different commercial carbonaceous substrates [3] showing optimal reproducibility and sensitivity. The obtained results in terms of dispersant ability were coupled with the study of the colloidal behavior of the dispersants in minimal and/or complete formulations establishing a structure-properties relation to explain the different dispersant capacity.



[1] M. Notari et al. WO2021205360A1; filing 14/10/2021
[2] R. E. Plotnick et al. Physical review E 53 (1996) 5461
[3] G. Ferraro et al. Energy Fuels 30 (2016) 9859

OR050

Structural Aspects of Metal-based Deep Eutectic Solvents and their Mixtures with Water

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Deep eutectic solvents (DESs) deal with mixtures of two or more compounds which, for a well-defined molar ratio, display a unique and minimum melting point that is not only lower than those of the single constituents, but also than the ideally predicted one, allowing the achievement of a liquid phase even from solid starting materials. This behavior relies on the extensive hydrogen-bond (H-bond) network established among the components, acting as H-bond donor (HBD) and H-bond acceptor (HBA) species. The complexity of the interactions formed in solution makes the achievement of a clear picture about the structural arrangement of these materials a fundamental knowledge to understand their physical-chemical properties and ultimately promote their applications.[1,2] In this framework, metal-based deep eutectic solvents (MDESs) can also be formed by combining a HBD with a metal salt. Besides intrinsic DES qualities like easy preparation, no need for purification, and tunable physical-chemical properties, MDESs also possess high polarity and great solvating capabilities due to the high concentration of ionic species, which make them ideal candidates as new electrolytes and media for electrodepositions and catalytic processes.[3] Here, we present our study about the structural characterization of MDESs formed by nickel, cobalt, and iron chlorides with common HBDs like urea and choline chloride. Some of these MDESs are formulated for the first time and we demonstrate that a liquid phase can be obtained only with the hydrated form of the metal salt. This opens the question about the role played by water in the eutectic formation and ultimately in its structural arrangement, which we unveiled with the employment of a combined approach exploiting molecular dynamics (MD) simulations, UV-Vis and near-infra-red (NIR) spectroscopies, small- and wide-angle X-ray scattering (SWAXS), and X-rays absorption spectroscopy (Figure 1). This multidisciplinary point of view allowed us to reconstruct the structural arrangement of the inspected MDESs and of their aqueous mixtures on both a short- and intermediate-scale level, clarifying the fundamental role of water in the eutectic formation and possibly challenging the definition at the base of these inherently complex systems.

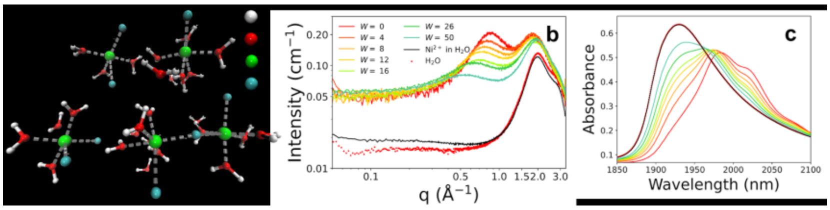

Figure 1. a) MD snapshot, b) SWAXS, and c) NIR spectra of NiCl2•6H_2O:urea:water 1:3.5:*W* mixtures.

[1] M. Busato et al. ACS Sustain. Chem. Eng. 9 (2021) 12252
[2] M. Busato et al. Phys. Chem. Chem. Phys. 23 (2021) 11746
[3] A. P. Abbott et al. Chem. Commun. (2003) 70

OR051

Can quantum-mechanical calculations shed light on cyclodextrin-based nanosponges (CD-NS) as drug delivery systems?

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In recent years, the interest in both the theoretical description and the structural modeling of cyclodextrin-based nanosponges (CD-NS) as carriers for a variety of guest molecules has risen. To this extent, previous studies have investigated the formation of non-covalent complexes between a guest molecule and β-cyclodextrin monomers, by applying different computational methods and different levels of theory. Among these, classical mechanics and semi-empirical levels were explored, as well as Density Functional Theory (DFT) methods, lastly.[1]

Due to the increasing complexity of these systems and their derivatives, especially considering β-cyclodextrin three dimensional networks, *i.e.,* nanosponges,[2] it is necessary to employ a method combining the accuracy of density functionals with the computational cheapness ensured by force-field-based methods and standard semi-empirical ones. A promising candidate, aimed at bridging this gap, is the recently developed semi-empirical xTB-GFN2 method, proposed by Grimme's group. xTB-GFN2 has been employed in a large variety of systems, including different host molecules.[3,4]

Among several possible pharmacologically active molecules, we have chosen melatonin and investigated the melatonin/β-cyclodextrin inclusion complex as a testing ground for this novel method.[5] Its validation has concerned structure, energetics, and IR spectra predictions in comparison with more standard DFT-based approaches. Specific attention has been paid to solvent effects, for water, with implicit and explicit solvation. The aim was to define a robust, accurate and, at the same time, low-cost methodology to investigate these complexes. So far, results have indicated that the xTB-GFN2 method provides accurate computed observables, paving the way for modeling cyclodextrin-based nanosponges.

[1] M. Nora et al. J. Incl. Phenom. Macrocycl. Chem. 96 (2020) 43
[2] F. Trotta et al. J. Org. Chem. 8 (2012) 2091
[3] C. Bannwarth J. Chem. Theory Comput. 15 (2019) 1652
[4] E. Boz Int. J. Mol. Sci. 22 (2021) 1
[5] R. Ferrero Molecules 26 (2021) 5881

OR052

Role of Dihydride and Dihydrogen Complexes in Hydrogen Evolution Reaction on Single-Atom Catalysts

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The hydrogen evolution reaction (HER) has a key role in electrochemical water splitting. Recently a lot of attention has been dedicated to HER from Single Atom Catalysts (SAC).[1] The activity of SACs in HER is usually rationalized or predicted using the seminal model proposed by Nørskov and co-workers in 2005,[2] where the free energy of an H atom adsorbed on an extended metal surface M (formation of a MH intermediate) is used to explain the trends in the exchange current for HER. SACs differ substantially from metal surfaces, and can be considered analogs of coordination compounds. In coordination chemistry, at variance with metal surfaces, stable dihydride or dihydrogen complexes (HMH) can form.[3,4] We show that the same can occur on SACs and that the formation of stable HMH intermediates, in addition to the MH one, may change the kinetics of the process.[5] Extending the original kinetic model to the case of two intermediates (MH and HMH) one obtains a three-dimensional volcano plot for the HER on SACs. DFT numerical simulations on 55 models demonstrate that the new kinetic model may lead to different conclusions about the activity of SACs in HER. The results are validated against selected experimental cases. The work provides an example of the important analogies between the chemistry of SACs and that of coordination compounds.

[1] L. Cao, Q. Luo, W. Liu, Y. Lin, X. Liu, Y. Cao, W. Zhang, Y. Wu, J. Yang, T. Yao, S. Wei, *Nat. Catal.* 2 (2019), 134.
[2] J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov, U. Stimming, *J. Electrochem. Soc.* 152, (2005), J23.
[3] G. J. Kubas, *Chem. Rev.* 107, (2007), 4152.
[4] R. H. Crabtree, *Chem. Rev.* 116 (2016), 8750.
[5] G. Di Liberto, L. A. Cipriano, G. Pacchioni, *J. Am. Chem. Soc.* 143, (2021), 20431.

OR053

Inkjet printing of photopolymerizable pullulan

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Pullulan is a linear exopolysaccharide naturally produced from starch by *Aurobasidium pullulans* and consisting of maltotriose repeating units. Thanks to its biocompatibility and biodegradability, this biopolymer has attracted significant attention for drug delivery [1] and tissue engineering applications [2]. The introduction of acryloyl moieties is a viably strategy for extending pullulan applicability also in additive manufacturing processes, such as visible stereolithography, two photon lithography [3] and inkjet 3D printing [4]. 3D printing is an emerging technique for the realization of 3D structures due to its ability to direct control shape, chemistry, and interconnected porosities. Methacrylated pullulan (PulMA) is a photopolymerizable pullulan derivative obtained by reacting pullulan with methacrylic anhydride in alkaline conditions. The synthetized product was investigated in terms of functionalization and cross-linking ability with a multi-technique approach (NMR, FT-IR, and Raman spectroscopy). The self-assembly properties of the pristine pullulan and PulMA solutions were investigated by means of phase-contrast microscopy and scattering of X-rays, revealing that both polymers form micrometric structures consisting of hydrated polymer chains assembled into swollen coils. The rheological properties were studied in view of using the aqueous solutions as inks for 3D printing, showing that the typical rheological behavior of pullulan is preserved in the PulMA derivative. The 3D printing process was optimized in terms of the processing parameter, producing self-standing printouts. The structural and mechanical properties of the 3D printed films were studied by Atomic Force Microscopy (AFM) and tensile strength tests, showing the presence of sub-micrometric phase segregated domains which are further separated by the cross-linking. As a result, the deformability of the materials is improved, with a lower tensile strength, most reasonably due to the spatial concentration of methacrylic units along the polysaccharide backbone.

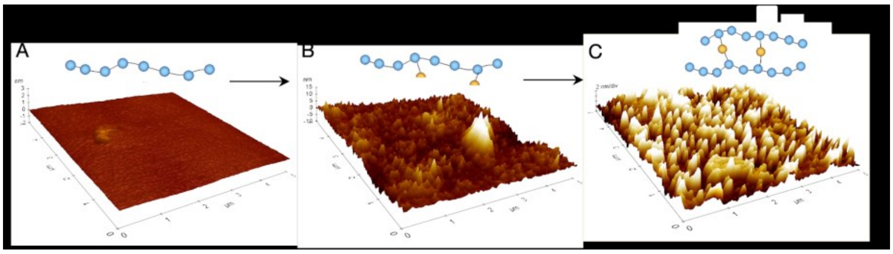

Figure. AFM images of Pul (a), PulMA (b) and PulMA_UV (c) 3D printed films.

[1] R. S. Singh et al. Carbohydr. Polym. 123 (2015) 190-207
[2] J. C. Fricain et al. Biomaterials 34 (2013) 2947-2959
[3] G. Della Giustina Mater. Des. 165 (2009) 107566
[4] G. Mugnaini J. Colloid Interface Sci. 592 (2021) 430-439

OR054

Why small proteins tend to have high denaturation temperatures

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Data indicate that small globular proteins (consisting of less than about 70 residues) tend to have high denaturation temperatures [1]. This finding is analysed by comparing experimental denaturation enthalpy and entropy changes of a selected set of small proteins with values calculated on the basis of average and common properties of globular proteins [2-4]. The conclusion is that the denaturation entropy change is smaller than expected, leading to an increase in denaturation temperature. The proposed molecular rationalization considers the existence of long-wavelength, low-frequency vibrational modes in the native state of small proteins due to their large surface-to-interior ratio. The effect of decreasing the conformational entropy gain associated with denaturation on thermal stability is directly verified by means of an already devised theoretical model [5,6].

[1] P. Leunberger et al. Science 355 (2017) eaai7825
[2] A.D. Robertson, K.P. Murphy, Chem. Rev. 97 (1997) 1251
[3] L. Sawle, K. Ghosh, Biophys. J. 101 (2011) 217
[4] G. Graziano, Phys. Chem. Chem. Phys. 22 (2020) 16258
[5] G. Graziano Phys. Chem. Chem. Phys. 16 (2014) 21755
[6] A. Pica, G. Graziano Biopolymers 105 (2016) 856

OR055

Biologically relevant colloidal hybrid calciprotein particles: effect of proteins and stabilizing agents on the formation and crystallization

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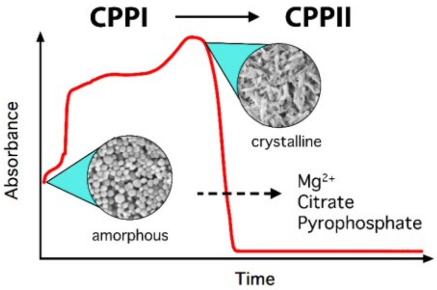
Despite the concentration of calcium and phosphate ions in serum is supersaturated with respect to hydroxyapatite, the precipitation of calcium phosphates (CaPs) is prevented by proteins which bind Ca^{2+} and phosphate ions or nascent CaP clusters and hinder the formation of calcifications that would lead to cardiovascular diseases [1]. Among them, the glycoprotein Fetuin-A (Fet-A) interacts with CaP amorphous clusters, resulting in colloidal protein-mineral hybrid complexes called "calciprotein particles" (CPPs) [2]. In pathological situations, the initially formed amorphous spherical nanoparticles (CPPI) may crystallize into secondary calciprotein particles (CPPII), which eventually lead to ectopic calcifications. Understanding from a physico-chemical perspective the mechanism of ripening of CPPI to CPPII and the factors affecting the process is thus fundamental to prevent the surge of vascular calcifications by developing strategies to delay the crystallization and precipitation of CaP in serum. In this contribution we inspect the effect of proteins (Fet-A and Albumin) and different ions (Mg^{2+}, pyrophosphate and citrate) on the formation and crystallization mechanism of CPPs [3]. Synthetic analogs of serum CPPs were initially prepared at different concentrations of Fet-A and their formation and ripening were followed *in situ* by means of turbidimetry and scattering techniques. The morphology of the obtained nanoparticles was investigated by means of electron microscopy whereas FT-IR spectroscopy and X-Rays diffraction allowed for the identification of the formed inorganic phases. Experiments were also conducted in the presence of different concentrations of albumin (the most abundant serum protein) and Mg^{2+}, pyrophosphate and citrate. This multi-technique approach allowed for the establishment of the most effective conditions for preventing the conversion of amorphous CPPI to crystalline CPPII, suggesting novel strategies to inhibit and treat cardiovascular calcifications.



[1] M.M.X. Cai et al. Bonekey Reports 4 (2015) 672
[2] W. Jahnen-Dechent et al. Journal of Structural Biology 212 (2020) 107577

OR056

Investigation of the effect of Li- and Al- co-doping on electrochemical properties of Li-rich transition metal oxides

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Lithium-rich transition metal oxides are considered a promising cathodic solutions in Li-ion batteries to meet the growing energetic demand, thanks to their high specific capacity and operational voltage[1-2]. Li-rich layered materials have a general stoichiometry $Li_{1+x}TM_{1-x}O_2$, in which TM is a blend of transition metals, as Ni, Mn, Co[2]. The presence of extra lithium ions within the transition metals layers allows to achieve a specific capacity between 200 and 250 mAh/g. Nevertheless, large irreversible capacity loss in the first cycle, poor rate capability, mean working potential decay upon cycling and cobalt content are still major drawbacks that are hindering commercialization. In order to make these materials up scalable to industrial production, it is important to consider the reduction of costs and the toxicity of raw materials, in particular cobalt. Cobalt reduction has been identified as major driver to improve the environmental benignity of batteries and the sustainability of the overall production-consumption-recycling lifecycle. Several efforts to reduce these problems have been made, including the development of different synthetic strategies, doping and surface modification. The most, widely explored, chemical strategy to mitigate the voltage decay and structural degradation in LRLO is the optimization of the transition metal blend. As an example, incorporation of redox inactive metals, such as Al, Zr, Ti, has been proposed in order to stabilize the lattice as well as the partial replacement of lithium ions with other alkali cations, e.g. K and Na; or doping the oxygen anion sublattice. In this communication, we present that the simultaneous replacement of cobalt in the layered structure with balanced amounts of aluminum and lithium, the latter exceeding the common 1.2 stoichiometry coefficient, leads to new stoichiometries with improved electrochemical stability. We report the characterization of these novel layered materials in terms of composition, structure, morphology and electrochemical performances in close comparison to the parent $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$. This approach can be applied to various Li-Rich materials as a strategy to mitigate the voltage decay and reduce the Cobalt content.

[1] Ji, X. et al. Journal of Power Sources 487, (2021).
[2] Zhao, S. et al. Angewandte Chemie - International Edition 60, 2208–2220 (2021).

OR057

Simulating Action-2D Electronic Spectroscopy of Quantum Dots: insights on the Exciton and Biexciton Interplay from Detection-Mode and Time-Gating

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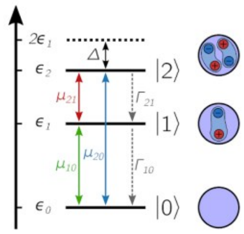
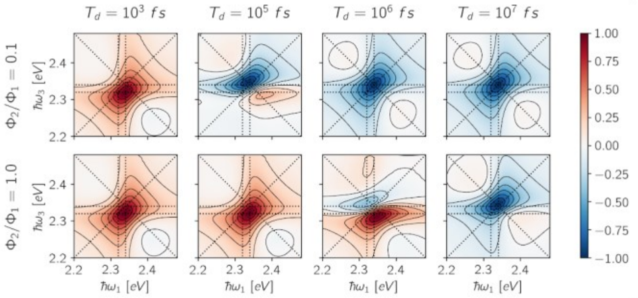
Action-2D Electronic Spectroscopy (A-2DES) is emerging as a powerful technique to investigate exciton dynamics. In this context, numerical simulations play a crucial role in aiding the interpretation of the spectral features, which often differ from those appearing in the analogous coherent technique [1]. In this work, we simulate the fourth-order response of a model semiconductor nanocrystal, focusing on the interplay between the exciton and the biexciton contributions to the A-2DES spectra [2]. The laser bandwidth is such that it selectively excites the band-edge 1S exciton, while the corresponding biexciton is generated by subsequent interactions and it may directly contribute to the signal according to its Quantum Yield (Fig. a). The simulation protocol is based on a non-perturbative solution of the Lindblad Quantum Master Equation, accounting for laser bandwidth and radiative/non-radiative relaxation processes [3]. The different contributions to the non-linear response are then disentangled using the Phase-Modulation scheme [4]. Firstly, we show how the active contribution of the biexciton to the measured signal can change qualitatively and quantitatively the 2D spectra, possibly inducing asymmetry in the maps and shifting the spectral features attributed to the single-exciton manifold (Fig. b). Since these effects depend not only on the biexciton photophysics but also on the nature of the detected signal, we consider both fluorescence and photocurrent detection-modes where different contributions from the exciton and the biexciton are expected [5]. Furthermore, we discuss the results obtained by integrating the spectroscopic output over a finite temporal window, which may be realized by time-gating of the measured signal [6]. Finally, we discuss how time-gating influences the spectral features and can be used to track dynamical aspects of the biexciton relaxation.

a)



b)



[1] O. Kuhn et al. J. Phys. Chem. Lett. 11 (2020) 838-842.

[2] S. Mueller et al. ACS Nano 15 (2021) 4647-4657

[3] F. A. Damtie Phys. Rev. A 95 (2017) 053830

[4] P.F. Tekavec et al. J. Chem. Phys. 127 (2007) 214307

[5] K. J. Karki et al. Nature Comm. 5 (2014) 5869

[6] P. Maly et al. J. Phys. Chem Lett. 9 (2018) 5654-5659

OR058

Raman amplification for trapped radiation in Si single nanoparticle

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We were able to study single silicon nanoparticles using micro-Raman spectroscopy. Si nanocrystal have been synthetized by an inductively coupled plasma chemical vapour deposition equipment, obtaining monocrystalline, isolated and monodisperse structures. Each observed crystalline particle has an octahedral shape of 100-200 nm (fig 1).

Single particle Raman scattering has been excited by using three laser wavelengths (532, 633 and 785 nm), finding an outstanding enhancement of the phonon signal compared to bulk. Such an intense signal amplification is attributed to multiple reflections during the radiation traveling path inside each nanoparticle [1,2]. Moreover laser beam induced thermal effects have been observed during the measurements at high laser fluences, some of them determining the entire particle melting. To better understand the behaviour of the electromagnetic field inside the nanocrystal, theoretical calculation of the electromagnetic field strength and it's propagation inside the nanostructure were carried out with a Finite Difference Time Domain method (FDTD)[3].

Photon trapping in a single Si nanoparticle could imply electron excitation enhancements from the valence to the conduction band since the photon energy largely exceeds the Si band gap and the evident electron concentration amplification in conduction band could be used to increment a photovoltaic current in a device of solar energy conversion.

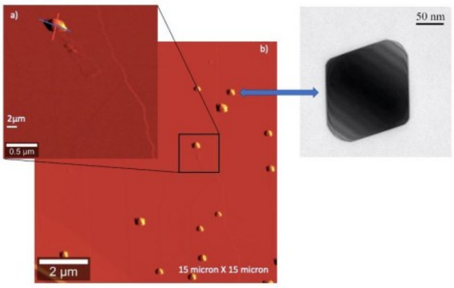

Fig. 1 :a) AFM and TEM image of Si nanocrystal, b) Raman spectra of Si bulk and single Si Nanocrystal

[1] G. Faraci, S. Gibilisco and A. R. Pennisi, Phys. Rev. B 80, 193410 (2009)
[2] E.M.L.D. de Jong et al. Sci. Rep. 6, 25664 (2016)
[3] Anwar, Farhana, et al. "." *Int. J. Renewable Energy Research* 7.2 (2017): 885-893.

A panoramic virtual tour in the world of knotted polyelectrolytes

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Topological constraints, and in particular knots, are ubiquitous in both natural (e.g., DNA and proteins) and synthetic polymers, and, in the last years, the convergence of theoretical and experimental studies has provided a wide number of striking examples of how chain-uncrossability defines an impressive range of polymer properties. For example, the presence of knots can endow polymer chains with peculiar relaxation kinetics or scaling behavior, and markedly affect their response to mechanical stretching and elongational flows, or their absorption into porous materials. Despite these promising results, the impact of knots on the properties of polyelectrolytes (i.e., polymers that carry on themselves charged, or chargeable, groups), has not been investigated as in depth as for their neutral counterparts.

Exploiting computer simulations, we show that knots markedly impact on the behavior of ring-shaped polyelectrolytes in diluted aqueous solutions, sometimes in very counterintuitive ways. Among our findings, we report that:

i. Weak (i.e., carrying weak acid or basic groups) polyelectrolytes show a non-monotonic trend of their size with respect to their ionization degree [1], a behavior that is in contrast with the expected swelling induced by ionization expected for unknotted species; this evidence is directly related to a depressed pK in the knot region, and to the fraction of counterions that can condense on the chain.
ii. By solely tuning the relative length of neutral and charged segments in block-copolyelectrolytes, one can achieve different combinations of the knot contour position and size [2]. Moreover, the latter can be also tuned by acting on solution properties such as solvent screening power or background salt concentration and valency.
iii. In presence of counterions with different radii, charged knots demonstrate to be able to selectively sequestrate the smallest species "tightening around them", and thus inducing a different ion partitioning along the chain contour.

In conclusion, knotted polyelectrolytes demonstrate, at least *in silico,* a very complex but promising stimuli-responsive behavior, and, consequently, a great potential that can be exploited for the production of advanced materials.

[1] A. Tagliabue, L. Izzo, M. Mella, J. Phys. Chem. B 2020, 124, 14, 2930–2937
[2] A. Tagliabue, C. Micheletti, M. Mella, ACS Macro Lett. 2021, 10, 11, 1365–1370

OR060

Immobilization of enzymes onto mesoporous silica nanoparticles to combat antibiotic resistance

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Antimicrobial resistance is a major concern that threatens human global health.[1] Due to the lack of new classes of antibiotics in the pipeline, drug delivery systems (DDS) provide a promising alternative to combat antibiotic resistance. [2] Advanced DDS based on nanoplatforms are under constant development. [3,4] Among drug nanocarriers such as dendrimers, lipid nanoparticles, gold nanoparticles and micelles, mesoporous silica nanoparticles (MSNs) are a promising option thanks to their easiness in functionalization and high surface area (up to 1400 m^2/g). [5] In the vast choice of MSNs functionalization, proteins such enzymes provide a suitable biocompatible moiety capable of interacting with bacteria cell wall. Based on this concept, herein, MSNs were functionalized with 3-aminopropyltriethoxysilane (APTES) to obtain MSN-NH_2. Subsequently MSN-NH_2 were modified with enzyme achieving MSN-lysozyme and MSN-*N*-aceltylglucosaminadase. The nanosystems were characterized by TEM, EDS, ζ-potential and DLS, ELS, FT-IR, TGA and elemental analysis, confirming the successful enzyme immobilization. Enzymatic activity of the immobilized enzymes was also verified. MSN-enzyme nanosystems were tested in planktonic against the Gram-positive bacteria, *Staphylococcus aureus.* MSN-lysozyme and MSN-*N*-aceltylglucosaminadase show antibacterial efficiency (in a concentration range of 12.5 to 200 µg/mL) reaching up to 80% of bacteria collapse in presence of MSN-*N*-aceltylglucosaminadase (150 µg/mL). Future work will be focused on the loading and the release of the antibiotic rifampicin to boost the antibacterial efficacy of the DDS and eradicate bacterial infection.

[1] WHO.Antimicrobial Resistance: Global Report on Surveillance;World Health Organization: Geneva, Switzerland, 2014.
[2] G. Bloom, G. Buckland, A. Wilkinson, V. Lin, S. Paulin, *BMJ Glob Health,* 2017, *2*, 000518
[3] R.R. Castillo, D. Lozano, B. González, M. Manzano, I. Izquierdo-Barba, M. Vallet-Regí. *Expert Opinion on Drug Delivery* 2019, *16*, 415.
[4] M. Vallet-Regí, Acta Biomater. 2022, 137, 44.
[5] M. Colilla, M. Vallet-Regí, Targeted Stimuli-Responsive Mesoporous Silica Nanoparticles for Bacterial Infection Treatment. *Int. J. Mol. Sci.* 2020, 21, 8605. RR. Castillo, M. Vallet-Regí, *Int J Nanomedicine*, 2021;*16*:4409.

OR062

Diffusive transport of micro-gel in transparent micron-sized porous hydrogel

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The diffusion of colloids through three-dimensional confining heterogenous matrices involves many attractive phenomena from physics to biology, applications from medicine to environmental science and geology representing a field of great interest. In order to completely understand and predict the relation between diffusion properties in confined conditions and the tortuosity of the confining matrix is required a deep characterization of the confining structure. The confining effects were recognized and well-studied in quasi-2D and highly ordered 3D matrix [1-2]. However, the extension of these approaches to anisotropic systems gave unsatisfying results. The prediction of particle transport in disordered porous natural media requires additional, significant efforts.

In order to relate the diffusion properties with the morphological features of the confining disordered matrices we developed 3D transparent porous hydrogels of poly(ethylene glycol) (PEG) [3]. The photo-polymerization of the diacrylate monomer (PEGDA), and the subsequent freeze-drying and rehydration of the resulting transparent hydrogel, allows the synthesis of the 3D porous network with tunable porosity at the micron scale with high transparency. The highly interconnected structure of PEG hydrogels with different monomer contents were characterized by laser scanning confocal microscopy. The precise geometrical and morphological characterization of the hydrogels' structure[3] revealed a complex, interconnected channel-like porous network having a smaller section ranging from 12 to 6 μm with the increasing of the monomer concentration in the pre-reaction mixture.

The confining effects imposed by the hydrogels were tested on thermos-responsive pNIPAM microgels (1.8 μm in diameter). Trajectories and mean square displacements obtained from particle tracking analyses highlight a slowdown of the microgels dynamics as a result on the increasing confinement degree. Thanks to the deep morphological and geometrical characterization, the extrapolated effective diffusivity coefficient and the diffusion exponent were related to the confinement length, the particle area fraction and the pore volume fraction of the confining hydrogels. The unusually pronounced dependence of the effective diffusivity on the pore volume fraction suggests microgel-hydrogel interactions. These results prove that the precise knowledge of the 3D porous network is crucial for the complete understanding of colloids' transport processes in disordered porous natural-like media. Our work represents an excellent starting point for the investigation of more complex system (i.e. bacteria) with interesting implication in colloids' filtration, anti-bacterial and anti-viral strategies and selective absorption.

[1] D. Nykypanchuk, H.H. Strey, D.A. Hoagland, Science (80-.). 297 (2002) 987–990.
[2] K. He, F. Babaye Khorasani, S.T. Retterer, D.K. Thomas, ACS Nano. 7 (2013) 5122–5130.
[3] G. Bassu, M. Laurati, E. Fratini, Colloid Surf. B submitted article.

OR063

Luminescent Eu:PO_4 - PVA dispersion for anti-counterfeiting inks

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Luminescent materials have found a wide range of applications in all walks of daily life, including advanced optical displays, solid state lighting, X-ray intensification, scintillation and many more. Recently, the lanthanide based luminescent nanostructures have been recognized worldwide for their better chemical and optical properties originating from their unique electronic structures as well as to their wide range of applications [1]. Ln-based light conversions, i.e., downshifting and up-conversion, have been adopted in commercial anti-counterfeiting [2,3] by the production of printable inks able to mark the objects and provide a refined way to increase the complexity level for authentication. The preparation of luminescent inks involves the formation of stable dispersions of luminescent powders into an organic polymer solution.

Here, the developing of luminescent inks based on Eu:YPO_4 nanopowders dispersed into polyvinyl alcohol (PVA) solution is reported. The nanopowders were prepared by precipitation followed by hydrothermal treatment in order to get an high size control of the particles. The preparation of dispersions involved a systematic study aimed to prepare a stable luminescent ink and, at the same time, to investigate the role of parameters affecting the stability and the efficiency of dispersion. In detail, the effect of polymer concentration for two different PVA (molecular weight and % of hydrolysis) was investigated for water and water/ethanol solution. The determination of chemical – physical properties, together with a spectroscopic and microscopic characterisation, allowed us to understand the kind of interactions involved in dispersion stability. Furthermore, the optimization of the concentration allowed us to obtain a dispersion, which can find application as anti-counterfeiting ink (Figure 1).

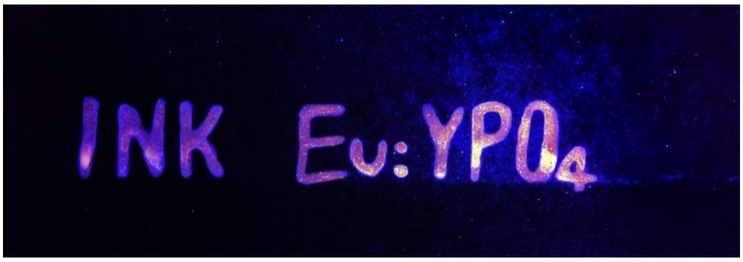

Figure 1. Ink 15%$_{w/w}$ Eu:YPO_4 in 10%$_{w/w}$ PVA 99+% hy under UV light (365 nm, 400W).

[1] Armetta, F., Saladino, M.L., Giordano, C., Defilippi, C., Marciniak, Ł., Hreniak, D., Caponetti, E. Non-conventional Ce:YAG nanostructures via urea complexes (2019) Scientific Reports, 9 (1), art. no. 3368.

[2] Suo, H. et al., High-security anti-counterfeiting through upconversion luminescence (2021) Materials Today Physics 21 100520.

[3] Huang, H. et al., Lanthanide-Doped Core@Multishell Nanoarchitectures: Multimodal Excitable Upconverting/Downshifting Luminescence and High-Level Anti-Counterfeiting (2020) Small 2000708.

OR064

Fluorescent Carbon Dots Enable Secure Communication Among Connected Implanted Medical Devices

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With diagnostic purpose, implanted biosensors can detect small variations in temperature that are a symptom of emerging infections; they can determine the presence of specific markers of pathologies, insert intelligent probes capable of detecting abnormal biochemical activities, etc. With therapeutic aims, sophisticated implantable biomedical devices can perform the direct and punctual release of drugs or microprobes capable of performing real localized operations with low invasiveness. What is missing is the interconnection among implanted biodevices. There is no platform to exchange information needed to turn the isolated biodevices into a part of a connected system that communicates, working in unison, under the control of a rational central system.

We will present a “revolutionary” digital communication platform based on molecular messengers to encode and transfer complex information across macroscopic scales through flowing fluids. We might call it the ‘next-generation of communication’, or n-G. We developed a secure communication platform based on Carbon Dots acting as chemical messengers for the secure transferring of information among implanted bio-devices through biological fluids. It mimics the standard communication system, based on electromagnetic waves, but it uses concentration pulses of nanoparticles released in the fluid by the transmitter. The corresponding chemical message is transferred by the flowing channel, and finally decoded by the receiver according to the fluorescence property of the Carbon dots.

The process is studied from a theoretical point of view by numerically solving the differential equation that governs the phenomenon. Theoretical results are exploited to develop a prototype n-G communication platform. The preparation of carbon dots, detailed characterization and implementation into the n-G communication platform will be presented.

OR065

Beyond entropy: understanding the stability of high entropy oxide $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$

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Since the discovery by Rost *et al*. of $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ as the first high entropy oxide (HEO) with rock salt (RS) structure, [**1**] the research on HEOs has been attracting increasing attention for different applications, such as Li-ion batteries, catalysis, etc.

We performed a systematic investigation of HEOs in the (MgCoNiCuZn)O family, unveiling the role of temperature and chemical composition in determining the stability of the single RS phase. This led us to question the concept that HEO $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ does form only because of a configurational entropy contribution: in fact, single-phase solid solutions (SSs) can be obtained moving from a 5- to a 2-component oxide as long as the molar fractions of ZnO and CuO are kept below a limiting value close to 0.2, which is dictated by the high-temperature solubility equilibria. Therefore, single-phase SSs can still be obtained by reducing the configurational entropy from 1.61R to 0.5R. We also demonstrate that the tendency of these SSs to distort from the cubic symmetry decreases with the configurational entropy, suggesting that the configurational entropy does not have the central role as stabilizing factor of the RS structure.

Then, we investigated the stability range of the HEO as a function of the chemical composition. Dealing with 5 cations, a systematic investigation would require a huge number of experiments. We tackled this problem using an approach based on experimental design, optimizing the compositions to investigate. The fraction of the RS phase was used as an input to build a model producing less than 50 samples, whose estimated fraction of RS phase was used as an input to describe the dependence of the RS fraction on the composition analytically.

This led us thus to identify the compositional domain of the RS phase, which appears to be larger for the Ni-rich ternary compositions than for the 5-element SS. Again, this points to limiting the role of entropy in stabilizing the (MgCoNiCuZn)O system.

Eventually, we used in situ synchrotron XRD to monitor the mechanism underlying the demixing of HEO upon temperature into different components. We demonstrated that Cu plays a crucial role, leading first to a tetragonal distortion of the cubic RS phase, then to the segregation of a Cu-rich guggenite phase, forming an intermediate layer between the original RS and the tenorite CuO phase. The prototype guggenite has the formula Cu_2MgO_3, though we found the Mg site can be shared by the other cations present in HEO. This mechanism contradicts the accepted view involving the segregation of single-parent oxides.

[1] C. Rost, E. Sachet, T. Borman, A. Moballegh, E. C. Dickey, E. C., D. Hou, J. L. Jones, S. Curtarolo, J.-P Maria. Nat. Commun. 6, (2015) 8485.

[2] M. Fracchia, M. Coduri, M. Manzoli, P. Ghigna, U. Anselmi Tamburini. chemrxiv, doi.org/10.26434/chemrxiv.14464980.v1. Accepted on Nat. Commun.

OR067

Operando and ex situ structural investigations of high entropy oxides as electrodes for Li-ion batteries

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High entropy oxides are gathering increasing attention in the search for new materials in a broad range of applications. Depending on the selected chemical composition and crystallographic structure, either anodes [1] or cathodes [2] for Li-ion and even Na-ion batteries [3] can be produced. Here we report on operando and ex situ investigations of anode $(Ni_{0.2}Co_{0.2}Mg_{0.2}Zn_{0.2}Cu_{0.2})O$ and cathodes $(LiFe_xMn_{2-x-y}Ti_yO_4)$ [2] for Li-ion batteries combining operando and ex situ XAS (X-ray absorption spectroscopy) and XRD (X-ray Diffraction). The prototype high entropy oxide $(Ni_{0.2}Co_{0.2}Mg_{0.2}Zn_{0.2}Cu_{0.2})O$ with halite structure underwent an operando XAS investigation with the aim of elucidating the working mechanism during the first lithiation/delithiation cycle. A complex redox mechanism was revealed, developing through the reduction of the transition metals, which triggers the conversion reaction below 1 V. The conversion is irreversible and incomplete, leading to the final collapse of the halite structure. However, the structure is retained up to the 60% of charge before collapsing, thus proving the beneficial role of the configuration entropy.[1] Multivariate curve resolution was employed as a novel strategy for XAS data processing. $LiFe_xMn_{2-x-y}Ti_yO_4$ and $LiFe_xCr_yMn_{2-x--z}Ti_zO_4$ were tested instead as cathodes. Compared to prototype $LiMn_2O_4$, the substitution of Mn with Fe, Cr and Ti suppresses the Jahn-Teller distortion, increasing the cycling voltage range (4.8-1.5 V), leading to higher capacity and significantly improved stability. XAS demonstrated that the only redox-active metal is Mn, while Fe, Cr and Ti are electrochemically inactive. XRD gave evidence of the formation of active Mn-rich and inactive Mn-poor domains, forming two separate spinel phases with different Mn:Ti ratios.[2] This is a different behaviour than the prototype compound, where J-T driven transformation of a tetragonal system occurs upon cycling. [5]

[1] P. Ghigna, et al., *ACS Appl. Mater*. Interfaces, 12, 45, 50344–50354 (2020)
[2] D. Callegari, et al., ChemRxiv, 10.26434/chemrxiv-2022-1xqnp
[3] C. Zhao, et al., *Angew. Chem. Int. Ed.*, 59, 264–269 (2020)
[4] F. Tavani et al., Chemical Physics Letters 760, 137968 (2020)
[5] R. Chen et al. *J. Phys. Chem. C* 118, 12608–12616 (2014).

OR068

Tuning the removal of copper ions with pH-responsive pHEMA/PAA hydrogels: implications in Cultural Heritage context

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The confinement of selective chelating agents inside hydrogels allows to obtain the gradual, controlled, and safe removal of corrosion layers from brittle and fragile bronze artworks, overcoming the limitations imposed by using traditional methods [1].

The addition of poly(acrylic acid) (PAA) in poly(2-hydroxyethyl methacrylate) (pHEMA) networks represents an improvement in the restoration practice of copper-based artworks thanks to the ability of PAA to give strong coordination bonds with metal ions *via* carboxylate groups in alkaline conditions [2].

Respect to previous pHEMA/poly(vinylpyrrolidone) (PVP) networks, using a scaffold already capable to interact with copper-based layers can increase the cleaning performances of the chelating solutions confined inside the hydrogel.

The progressive deprotonation of carboxylic groups in PAA in high alkaline conditions, and the subsequent increase of the electrostatic repulsion between the polymeric chains, leads to an increase of the gels porosity at the micro- and nanoscale, as confirmed by small angle X-ray scattering (SAXS) and scanning electron microscopy (SEM) analysis. The increase of hydrophilic moieties as a function of pH was also confirmed by Differential scanning calorimetry (DSC), thermogravimetric (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

The Cu(II) ion adsorption kinetics of pHEMA/PAA networks at different pH values were investigated and compared with that of pHEMA/PVP, highlighting the effect of the gels' structure and functional groups on the adsorption process.

To treat real corrosion patinas, pHEMA-based systems were uploaded with tetraethylenpentamine (TEPA), a chelating agent whose copper (II) complex has a stability constant four orders of magnitude higher [3] than that of other traditional chelators used by conservators.

Upon application of the gels loaded with TEPA onto corroded bronze, copper oxychlorides dissolve and migrate inside the gels, where Cu(II) ions form ternary complexes with TEPA and carboxylates in PAA. The removal of oxychlorides is more effective and faster for pHEMA/PAA than its /PVP counterpart. The selective action of the gels preserved the cuprite layers that are needed to passivate bronze against corrosion, and the pH-responsive behavior of pHEMA/PAA allows full control of the uptake and release of the Cu(II)–TEPA complex, making these systems appealing in several fields even beyond Cultural Heritage conservation (e.g., drug delivery, wastewater treatment, agricultural industry, and food chemistry).

[1] A. Scott, Copper and bronze in art, (2002), 352-397, The Getty Conservation Institute, Los Angeles
[2] N. Sebastian et al., Polym. Degrad. Stab., (1998) 5
[3] A. Martell, Ed., Critical Stability Constant - Vol. 2: Amines, (1975) Springer US

OR069

Common mistakes in the analysis of thermodynamic and kinetic data appearing in the environmental adsorption literature

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For decades, adsorption has attracted the attention of many researchers worldwide, resulting in the publication of a considerable number of adsorption studies, especially recently focused on the application of adsorptive removal of pollutants from aqueous solution.

Here we discuss some incorrect results and statements frequently found in the scientific environmental adsorption literature. In particular, we focus on the thermodynamic and kinetic aspects of the adsorption process, including erroneous calculation of the equilibrium constant, inaccurate calculation of ΔH° and ΔS°, mismatch between selected isotherm models and isosteric heat of adsorption, misleading interpretation of the spontaneity of a process, erroneous identification of the best-fitting kinetic model [1-3].

[1] S. Salvestrini et al. J. Mol. Liq. 352 (2022) 118762
[2] S. Salvestrini et al. J. Chem Thermodyn. 68 (2014) 310-316
[3] S. Canzano et al. Ads. Sci. Technol. 30, (2012) 217–225

OR070

Phase separation behavior and structural role of amylose and amylopectin in PVA/starch hybrid networks: taking a step back to gain broader perspectives.

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The constant increase in production, use, and disposal of synthetic plastic represents a concerning threat to the sustainability of our ecosystem. A possible strategy to reduce the consumption of synthetic polymers is to blend them with available natural products. A well-established couple for the production of biocomposite plastic materials is represented by Poly(Vinyl-Alcohol) (PVA) and starch. Nevertheless, the interactions between PVA and starch's polymeric components (amylose and amylopectin) are still a matter of debate. In this contribution, we prepared and analyzed simple PVA/amylose, PVA/amylopectin, and PVA/amylose/amylopectin systems in order to formulate a wider theoretical framework that describes said interactions and their consequences on the features of PVA/starch-based materials. Investigation of PVA/amylose, PVA/amylopectin, and PVA/amylose/amylopectin systems with variable PVA/polysaccharide ratios allowed a deeper understanding of the possible evolution of a real PVA/starch cryogel. Thanks to Confocal Laser Scanning Microscopy (CLSM) on pre-gel fluorescently labeled solutions, we determined the absence of miscibility between PVA and amylose, as well as PVA and amylopectin, in the considered temperature range (25-98°C). In PVA solutions, amylose shows a supramolecular arrangement, reasonably corresponding to single helixes forming liquid crystals with nematic order. Instead, PVA and amylopectin solutions show liquid-liquid phase separation.

In the cryogels, for PVA:polysaccharide ratios of 2:1, the heteropolymeric interactions are strongly unfavored, whereas PVA-PVA interactions are increased, leading to the formation of more compact and crystalline PVA networks. The maximum extent of PVA polysaccharide interactions is likely to occur at a 1:1 ratio. Nevertheless, PVA amylopectin interactions are "destructive", given the inability of amylopectin to form proper networks, while PVA-amylose interactions can be "constructive" and lead to the formation of hybrid tie points in the gel, containing both the polymers in strong association, as suggested by Differential Scanning Calorimetry (DSC) and Small Angle X-Ray Scattering (SAXS) measurements.

As an example of the implications that this broader knowledge could have, we provided a prevision of the variation of one simple parameter (the gel fraction) for any possible PVA/amylose/amylopectin mixing ratio and preliminarily tested its validity on a real PVA/starch sample.

OR072

Fluorinated Nanomaterials as Powerful Tools in Medicine

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This work addresses the current need for novel sensitive, robust, and selective diagnostic tools for non-invasive in vivo imaging, which are able to improve the medical practice through earlier diagnosis of disease, implementation of targeted therapies, and localization of diseased tissues. Our approach is based on the development of sustainable fluorinated probes enabling ^{19}F-MRI, as a complementary tool, to be coupled with other diagnostic imaging techniques such as ^{1}H-MRI, Raman and fluorescence imaging, in order to overcome their present shortcomings. This talk reports about a unique fluorinated imaging agent (PERFECTA) bearing 36 equivalent ^{19}F atoms and therefore showing a single, intense ^{19}F-NMR signal. Biocompatible nanoformulations of PERFECTA demonstrated excellent cellular compatibility and spectral properties (relaxation times and sensitivity) adequate for in vivo ^{19}F-MRI use (Figure 1) [1-2]. In this presentation PERFECTA ability to work as multiscale and multimodal probe will be shown [3]. Moreover, effects of fluorination on self-assembly of PERFECTA amphiphilic derivatives [4] will be also presented as well as their biological interactions and response.

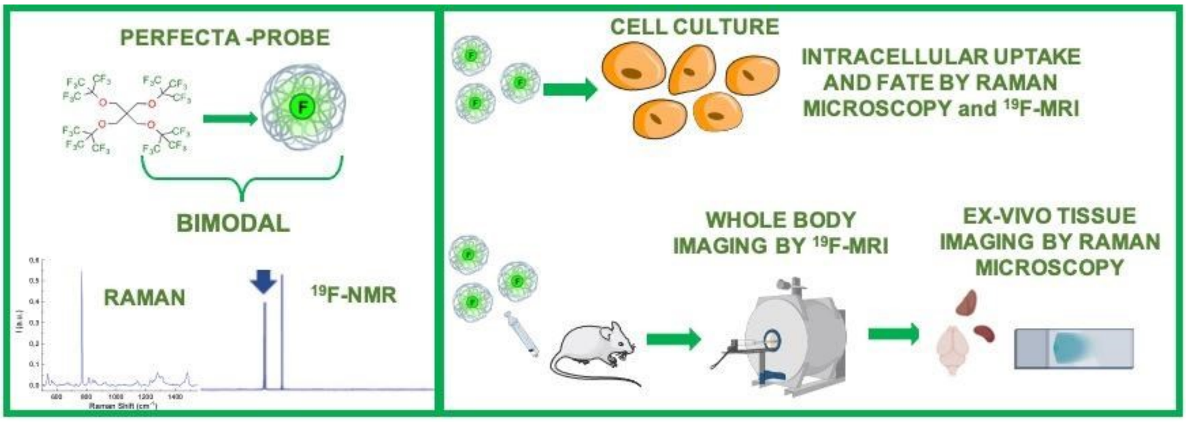

Figure 1. (Left) Molecular structure of PERFECTA and schematic drawing of a representative nanoparticle (F-NP) containing it. Typical Raman and ^{19}F-NMR spectra of PERFECTA NP dispersions. (Right) Representative scheme of F-NP applications in medicine as diagnostic tool for ex-vivo and in vivo cell labelling .

[1] I. Tirotta et al. J. Am. Chem. Soc. 136 (2014) 8524
[2] C. Chirizzi et al. Radiology 291 (2019) 351
[3] C. Chirizzi et al. J. Am. Chem. Soc. 143 (2021) 12253
[4] M. Rosati et al. Macromolecules (2022) https://doi.org/10.1021/acs.macromol.2c00129

OR073

Electrochemical characterization of the SOEC electrolyte-air electrode interface fabricated by femtosecond laser micromachining

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High-temperature solid oxide electrolysis cells (HT-SOEC) are one of the most promising technologies for the production of green hydrogen. Most of the optimization efforts are concentrated on the electrodes, where electrochemical reactions involve ionic species, electrons and gas molecules. In addition to composition, microstructure significantly contributes to the efficiency of electrodes. Porous composite structures made of homogeneous mixture of two solid phases and pores have been widely investigated and still represent state-of-art of the HT-SOEC electrodes. Computational studies found that non-homogenous spatial distribution of solids and pores may positively affect the performance, thanks to increased length of interfaces and optimized diffusion length [1,2].

The novelty of the work is the deposition of a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) porous electrode over $Ce_{0.8}Sm_{0.2}O_{1.90}$ (SDC) dense electrolyte with a columnar shape prepared by femtosecond laser micromachining (FLM). Scanning electron microscopy (SEM) and white light interferometry (WLI) images of patterned SDC surface indicate that the columnar electrolyte are dense cylinders 20 µm wide, 40 µm high and separated from each other by (i) 40 or (ii) 80 µm (see Figure 1).

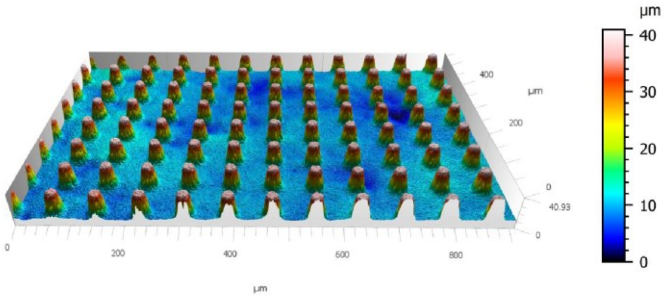

Figure 1. WLI image of patterned SDC electrolyte with 80 µm spacing.

The electrochemical behavior of half-cells with patterned working electrode was tested by electrochemical impedance spectroscopy (EIS) at constant temperature (600 °C) for >100 hours, in order to determine the polarization resistance (R_p). In addition, half-cell with flat working electrode was also measured as a reference. A significant decrease of R_p was observed respect to the reference, although associated to progressive degradation of performances.

[1] Delloro, F. & Viviani, M. Simulation study about the geometry of electrode-electrolyte contact in a SOFC. *J. Electroceramics* **29**, 216–224 (2012).

[2] Cebollero, J. A. *et al.* Optimization of laser-patterned YSZ-LSM composite cathode-electrolyte interfaces for solid oxide fuel cells. *J. Eur. Ceram. Soc.* (2019). doi:10.1016/j.jeurceramsoc.2019.02.049

OR074

An operando SAXS/WAXS study on the full reversibility of aluminium graphite dual ion cells

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Aluminium graphite dual ion cells (AGDICs) have attracted significant interest as a potential electrochemical storage system characterized by high power and elevated cycle life.[1] The characteristics of the AGDICs make them particularly suitable for applications in stationary storage systems, where long cycle life and low cost is highly desirable.

Herein we investigated the reaction mechanism of the aluminium graphite dual ion cell by operando X-ray scattering from small angles (SAXS) to wide angles (WAXS). The staging behaviour of the graphite upon cycling was evaluated by measuring the repeated intercalation distance in the small-angle range, along with the mesoporosity of the cathode graphite upon cycling. The investigation demonstrated complete reversibility of the electrochemical intercalation process, alongside nano- and micro-structural reorganization of natural graphite induced by intercalation in the first cycle with an associated increase in the electrode mesoporosity.

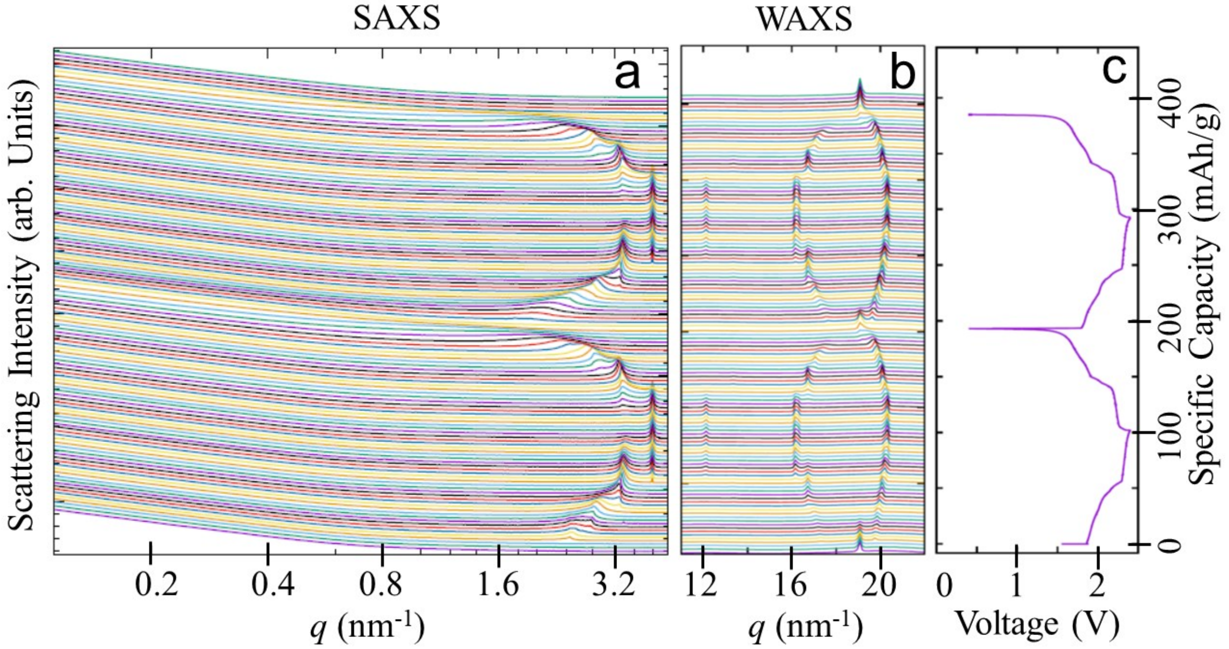

Figure 1. Evolution of the operando WAXs and SAXS patterns of graphite in an aprotic aluminum battery.

[1] Muldoon, J., Bucur, C. B., & Gregory, T. (2014). Quest for nonaqueous multivalent secondary batteries: magnesium and beyond. *Chem. Rev.*, *114*(23), 11683–11720. https://doi.org/10.1021/cr500049y

Magnetic Interactions and Reversal Processes in Ferrites-Nanocomposites

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Magnetic interactions are the key to the efficiency of magnetic nanomaterials in several industrial applications, such as magnetic recording media and permanent magnets [1]. In this regard, functional oxide nanocomposites (NCs) revealed their potential applicability, owing to the combination of two or more prototypical phases which results in novel systems with tunable properties. Among nanostructured materials, M-type hexaferrite $SrFe_{12}O_{19}$ (SFO) has become extremely appealing for the advancement of NCs [2,3]: a size reduction of such particles yields the formation of single-domain state below a critical value, which results in an increase of magnetic anisotropy and thus coercivity (H_c). However, many factors, e.g., size, shape and interphase conditions, affect the energy barrier distribution, and deserve careful consideration, as consequently influence the magnetization reversal mode. Additionally, the inclusion of another magnetic phase makes the analysis of the interphase exchange-mechanism more complex, and difficult to be quantified. In a recent work, a set of magnetic NCs have been investigated, with specific focus on the degree of magnetic coupling that can be achieved at the inter-phase between SFO and $CoFe_2O_4$ (CFO) phases [4]. The structural, morphological and magnetic characterizations confirmed that by controlling the size and distribution of both phases, resulted in an efficiently coupled system. This was evinced by the analysis of the irreversible component of the susceptibility (χ_{irr}) obtained by the switching field distributions (SFD), which clearly showed a single reversal process of magnetization. Since effects owed to complex magnetic structures may be overlooked in SFDs, especially in composite materials, we have investigated more in-depth the reversal mechanism by performing magnetic relaxation measurements in a reverse field (H_{REV}) after saturation in a given direction. From the magnetic viscosity (S) extracted from those measurements, the activation volume (V_{ACT}) [5] was estimated: our results provide evidence that the magnetization reversal process of the NCs is strongly dependent on the interphase exchange interaction. To validate this method the magnetization reversal was investigated by collecting first order reversal curves (FORCs). In conclusion, our work reveals the feasibility of activation volumes´ analysis to assess inter-grain interactions in ferrites-based NCs. We thank the Swedish Energy Agency and Swedish Research Council (VR) for financial support.

[1] J. Liu Et al. Nanoscale Magnetic Materials and Applications, Springer 11 (2009) 309
[2] C. de Julián Fernández et al. J. Phys. D: Appl. Phys. 54 (2021) 153001
[3] P. Maltoni et al. Sci. Rep. 11 (2021) 23307
[4] P. Maltoni et al. J. Phys. Chem. C. 125,10 (2021) 5927
[5] S. Laureti et al. Nanotechnology 21 (2010) 315701

OR077

On the Complex Interplay between Charge Injection, Electron Transport, and Quantum Efficiency in Ambipolar Trilayer Organic Light-Emitting Transistors

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Organic light-emitting transistors (OLETs) are optoelectronic devices capable to show light emission from a single device structure endowed with intrinsic electrical switching capability. Therefore, OLETs are multifunctional, light-emitting, and ambipolar devices suitable for a wide variety of applications, ranging from displays to sensors. However, the difficulties in fully understanding the complex interconnection between electroluminescence and ambipolar charge transport properties have collided with the limited availability of electron transport semiconducting materials, with a consequent lack of systematic investigations aiming at developing the OLET structure. Here, through the selection of compounds with tailored chemical structures, we unraveled the complex correlation between energy level alignment within the structure, morphological properties, and intrinsic characteristics of the electron transport semiconductor.[1] In this context, the introduction of a proper electron injector at the emissive/semiconducting layers interfaces further highlighted the bidimensional nature of OLETs with respect to the one-dimensional operation of prototypical organic light-emitting diodes.

[1] S. Moschetto, E. Benvenuti, H. Usta, R. Ozdemir, A. Facchetti, M. Muccini, M. Prosa, and S. Toffanin, Adv. Mater. Interfaces 2022, 9, 2101926.

OR081

The Time Scale of Electronic Resonance in Oxidized DNA

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It is shown that the yields of oxidative damage observed in double-stranded DNA oligomers consisting of guanines separated by bridges of various lengths and compositions are reliably accounted for by a multistep kinetic mechanism, in which transient and non-transient electronic resonances induce charge transport and solvent relaxation stabilizes the hole transfer products [1]. The kinetic constant for the charge transfer step is computed by solving the time dependent Schrodinger equation adopting a basis set of vibronic states with the hole localized on a single nucleobase. Our mechanism makes use of solid experimental data: the kinetic constant for the deprotonation step of ionized guanine and the relaxation time of the solvent. However, the time needed to bring donor and acceptor sites into resonance, thus activating the hole-transfer dynamics, is a quantity extremely difficult to achieve by direct observation [2], so that it has been treated as an adjustable parameter.

In order to compare theoretical predictions with the experimental results, the set of ordinary differential equations (ODEs) of the kinetics is solved and the yield ratios of damaged products are computed. Interestingly, the resolution of the ODE equations indicates that the optimum value for the activation time is almost independent of the nature and the length of the DNA sequence. Indeed, a single value, amounting to ca 100 picoseconds, was found to ensure an excellent agreement between predicted and observed damaged product ratios for all the investigated DNA sequences.

Additional MM simulations followed by QM/MM calculations including explicit solvent molecules found the solvent response to take ca 500-700 picoseconds to bring two guanines, i.e., the sites with the lowest ionization energy, into resonance. That range of values in reasonable agreement with the estimate previously obtained by using the kinetic model [3].

Our investigation demonstrates that microscopic coherence is crucial for rationalizing the observed yield ratios of oxidative damage to DNA. Interference among probability amplitudes of indistinguishable electron-transfer paths can drastically change the outcome of charge transport, even in DNA oligomers constituted by similar building blocks, and allows for reconciling apparently discordant experimental observations, as shown by the excellent agreement between experimental and predicted damage yield ratios.

Therefore, properly tailored DNA oligomers appear to be a promising workbench for studying tunneling in the presence of dissipation at the macroscopic level [4].

[1] A. Landi, R. Borrelli, A. Capobianco, A. Peluso. J. Phys. Chem. Lett. 10 (2019) 1845
[2] A. D. Levine, M. Iv, U. Peskin. Chem. Sci. 7 (2016) 1535
[3] A. Landi, A. Capobianco, A. Peluso. Molecules 26 (2019) 5497
[4] A. Landi, A. Capobianco, A. Peluso. J. Phys. Chem. Lett. 11 (2020) 7769

OR082

New Descriptors for model Electrocatalysts: Metal Porphyrins Explored by Electrochemical Scanning Tunnelling Microscopy

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M-N-C single site catalysts are nowadays intensively investigated as promising candidates to replace Pt group metals in a variety of electrocatalytic reactions, for example the O_2 reduction reactions (ORR). M-N_x sites exhibit good catalytic properties, but there still is a lack of understanding of the precise configuration of the M-N_x single site especially during the catalytic process. On this regard, metal porphyrins are good model systems for mimicking M-N_4 sites [1-3]. In this work EC-STM was employed for the investigation of ORR at metal centered octaethylporphyrins. In particular the absorption of O_2 is observed from STM imaging as a protrusion (ΔZ) with respect the non-coordinated metal center and ΔZ was considered as a parameter for describing the electrocatalytic process (Fig. 1a,b).

For those metal-centered molecules exhibiting a redox couple, the ORR occurred within a redox-like catalysis, where the metal center mediates the reduction of the oxygen molecule, recovering its original oxidation state by reduction at the electrode (Fig. 1c,d). Conversely, molecules without a redox behavior did result in worse performances, but a certain catalysis was still observed such as Pt or Cu OEP. According to the simple Sabatier's principle, a good catalyst should bind reactants neither too strongly nor too weakly, and the same is valid for reaction products. Transferring this concept to the volcano-plot of Fig. 1e, where $E_{p/2}$ is plotted versus ΔZ, Co and Fe could be related to an intermediate binding strength, while Pt and Mn could be associated to strongly binded O_2. This leads to the assumption that ΔZ can be assumed as an independent descriptor of the catalytic behavior of a single site catalyst.

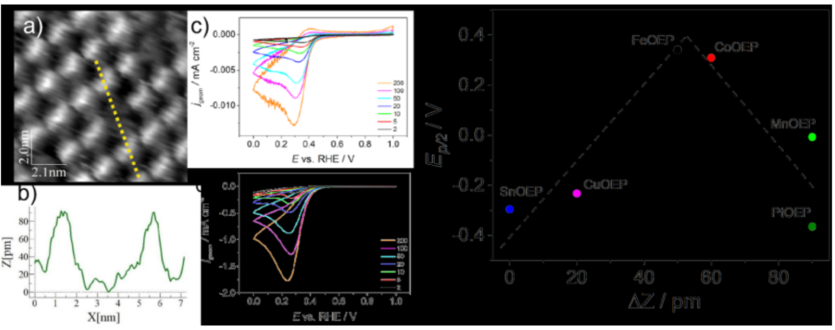

Figure 1. Figure 1 a) Potentiodynamic EC-STM images of a mixed H_2OEP / FeOEP adlayer adsorbed on HOPG in O_2 saturated 0.1 M $HClO_4$. b) topographic profiles corresponding to the yellow dashed; CV of FeOEP @ HOPG in c) Ar purged and d) O_2 saturated 0.1 M $HClO_4$, e) correlation of the STM revealed protrusion and the half-peak potential for all the investigated metal porphyrins.

[1] Zagal, J. H.; Koper, M. T. M. Angew. Chemie - Int. Ed., 2016, 55 (47), 14510.
[2] Facchin, A.; Zerbetto, M.; Gennaro, A.; Vittadini, A.; Forrer, D.; Durante, C. ChemElectroChem, 2021, 8 (15), 2825.
[3] Facchin, A.; Kosmala, T.; Gennaro, A.; Durante, C. ChemElectroChem, 2020, 7 (6), 1431.

OR083

The role of F•••F interactions in supramolecular networks

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Despite displaying energetically weak Van der Waals attractive interactions, fluorine-fluorine contacts, when arranged in super-fluorinated complexes, can cooperate and highly stabilize supramolecular networks. In a tight collaboration with several experimental groups, we were able to investigate the stability of various novel super-fluorinated complexes and to rationalize the role of fluorine-fluorine interactions in their self-assembly processes exploiting different computational levels of theory at various length- and time-scales. Here we present an overview of our most significant results and current applications.

By means of a DFT study, we have electronically characterized the nature and the strength of non-covalent interactions of a hyper-fluorinated gold nanocluster bearing 486 F atoms. An accurate mapping of the inter- and intra-interaction energies combined with the investigation of the electron density distribution between all possible F•••F contacts present in the crystallographic structure allowed us to confirm the attractive and additive nature of fluorine-fluorine interactions and their role as a driving force for crystal packing. [1] We used the same electron density distribution analysis, based on bond-order and non-covalent interaction mapping, to explore the nature of the stabilizing interactions between PFTB-L-DOPA (3,4-dihydroxy-L-phenylalanine fluorinated with perfluoro-tert-butoxy) with PEDOT:Nafion complexes, the latter an ideal candidate for neural recording and stimulation applications.

We also investigated the morphological supramolecular assembly of originally synthetized super-fluorinated Janus dendrimers in water with different organic co-solvents by means of a multi-scale computational approach. All-atoms molecular dynamics of dimers in explicit solvent revealed the existence of different conformations for dendrimers depending on the type of the organic co-solvent and allowed to derive accurate parameters for successive coarse-grain simulations. Such simulations demonstrated how the morphology of the final aggregate derives from a fine balance between fluorophobic effect and hydrogen bonds between dendrimers and the co-solvents. [2]

We are presently applying the same multi-scale approach to study the self-assembly of novel ABC copolymers bearing a hyper-fluorinated block and their morphological aggregation in water.

[1] C. Pigliacelli et al. Nat. Commun. (accepted on 7th April 2022)
[2] M. Rosati et al. Macromolecules 55 (2022) 2486

OR084

Bright orange and green emission in 2D Mn-based Hybrid Metal Halides

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Starting from the well-studied $APbX_3$ (A = $CH_3NH_3^+$, Cs^+; X = Cl^-, Br^-, I^-) perovskite, new derivates can be obtained with the partial or full substitution of the A cation with different ions [1]. The introduction of larger or smaller cations in the A site favors the formation of polymorphs of a lower dimensionality (2D or 0D). To date, one of the most promising strategies to tune and confer excellent optoelectronics is the insertion of an organic cation instead of an inorganic one. The resulting structures are named "hybrid metal halides" [2]. Promising compounds can be obtained starting from the emissive Mn- based stoichiometries $AMnX_3$, of which $CsMnBr_3$ constitutes an interesting red-emissive material having a PLQY of 54% [3]. Here, we present our recent results achieved in the preparation of emissive 2D Mn-based hybrid metal halides as single crystals. Starting from the reported synthesis of $CsMnBr_3$, the Cs^+ was progressively substituted with the butylammonium ($BA^+ = C_4H_{12}N^+$) cation, leading to a phase with a different crystal structure presenting an orange emission. The obtained sample crystallizes giving white millimeter-sized layers, composed by agglomerates of single crystals, as observed from the SEM micrographs. By the preliminary analyses, the structure consists of monolayers of connected $[MnBr_6]$ octahedra stacked by two BA^+; the compound crystallizes in the orthorhombic system and presents the BA_2MnBr_4 stoichiometry. Moreover, the BA^+ cation is progressively replaced by methylammonium ($MA^+ = CH_6N^+$) cation, to study the possibility to form an alloying between BA – MA. Increasing the amount of MA^+, a new distinct phase is formed, still under investigation, with an interesting green emission. The synthesis used for both the compositions is based on the dissolution of the precursors ($MnCO_3$ and MABr or BABr) in an acid media (HBr), followed by the slow solvent evaporation. The characterization of these materials was carried out using SEM, TEM, XRD, FTIR, DTA-TG coupled with GC-MS, and optical analyses (ABS, PLE, PL, PLQY, TrPL).

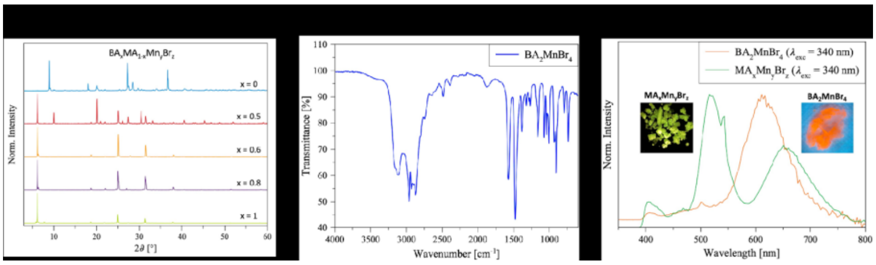

Figure: (a) Experimental powder patterns of the samples with $BA_xMA_{1-x}Mn_yBr_z$ composition. (b) FTIR spectra of BA_2MnBr_4. (c) PL spectra with images under UV lamp (λ = 365 nm) of crystals' $MA_xMn_yBr_z$ and BA_2MnBr_4.

[1] T.J. Milstein et al. Nano Lett. 18 (2018) 3792–3799
[2] Q.A. Akkerman. ACS Energy Lett. 5 (2020) 604–610
[3] J. Almutlaq et al. ACS Mat. Lett. 3 (2021) 290–297

OR085

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskites for application in intermediate-temperature solid oxide fuel cells: effect of morphology on crystal structure, microstrain, and electrochemical properties

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Mixed ionic-electronic conductors (MIECs) are widely used as electrodes in solid oxide fuel cells (SOFCs). Among these, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ perovskites are extensively studied as cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC), due to their high ionic-electronic conductivity, good structural stability, and high electrochemical activity for the oxygen reduction reaction [1]. Among the possible compositions, the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) is one of the most used. Morphology strongly influences electrode performance. Recent studies demonstrate the superior electrochemical performance of nanofibers compared with granular materials and nanorods of similar size [2,3], essentially due to longer charge conduction paths and reduced bottlenecks. Electrospinning is an efficient process to fabricate nanofibers. It is based on a high-voltage power applied between a precursors solution and a metal collector, where the fibers are deposited [4]. For the present experiments, LSCF electrospun nanofibers were prepared after careful optimization of the equipment operating parameters [5]. For the aim of comparison, LSCF commercial powders (Sigma-Aldrich) were considered as well. A structural and microstructural study was conducted to unveil correlations between morphology, crystal structure, and oxygen transport properties. Both nanofibers and powders were analyzed by synchrotron X-ray diffraction at room and high temperature, and by micro-Raman spectroscopy. A particular effort was made to investigate the rhombohedral to cubic phase transition of LSCF, demonstrating a different transition temperature for the two different morphologies. Furthermore, by applying Rietveld method to the diffraction data, detailed information about the crystal structure was obtained, and the trends of oxygen site occupancy, cell parameters, average atomic volume, and atomic displacement parameters were evaluated as a function of temperature for both nanofibers and powders. A large amount of microstructural information were gained by analyzing the peaks broadening. Structural and microstructural results were correlated with electrochemical impedance spectroscopy measurements (EIS) performed on LSCF electrodes. The two main contributions resulting from EIS data, *i.e.* the Gerischer and the CPE polarization resistance components, varied with temperature, and their changes were consistent with the modifications occurring in the crystal structure.

[1] S. P. Jiang, Int. J. Hydrogen En. 44 (2019) 7448.
[2] A. Enrico et al. J. Eur. Ceram. Soc. 38 (2018) 2677.
[3] P. Costamagna et al. Metal Oxide-Based Nanofibers and Their Applications Ch. 13 (2022) 301-331.
[4] J.-S. Park, Adv. Nat. Sci: Nanosci. Nanotechnol. 1 (2010) 043002.
[5] A. Enrico et al. Fuel Cells 17 (2017) 415.

OR086

Pt-based complexes as single site catalysts towards ORR: an EC-STM approach

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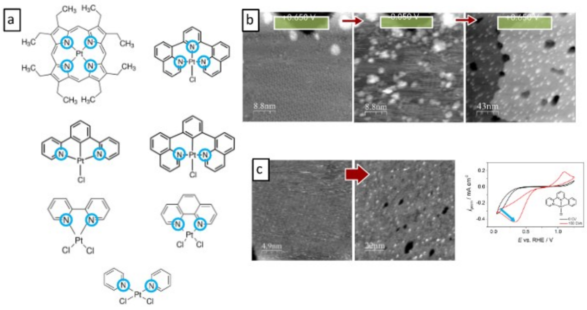
Oxygen reduction reaction (ORR) is a vital reaction, not only for all biological systems on earth, but also in the emerging field of fuel-cells and metal-air batteries. In these devices, O_2 is entailed at the cathode, and it undergoes reduction, with H_2O or H_2O_2 being produced. Unfortunately, ORR kinetics is sluggish and needs to be catalyzed. [1] Though platinum group materials (PGM) should be avoided due to scarcity and high costs, they still represent the most performing catalysts for ORR. EC-STM can be conveniently employed as an advanced *in situ* characterization technique, which provides information on a sample surface at the solid/electrolyte interface. Indeed, the sample is probed by STM and at the same time is polarized as working electrode. This means that EC-STM can record the dynamic of an electrocatalytic process at the atomic scale [2,3]. This ability was exploited to characterize a series of platinum-based molecular complexes, as shown in figure 1.a. The peculiarity is that each complex carries a different number of coordinating nitrogen atoms, and the resulting electrochemical activity towards ORR significantly differs among different complexes. All the complexes have no redox behaviour, but in presence of O_2 species, a relevant catalytic behaviour emerged, in particular after repetitive potential scanning by cyclic voltammetry. (figure 1.b). The surface morphology appeared to change after this potential cycling (figure 1.b,c), thus pointing out the role of defects and molecular aggregation in the final electrocatalytic performances. A product selectivity trend was also revealed by means of rotating ring and disk technique.



[1] J. H. Zagal, F. Bedioui, Electrochemistry of N4 Macrocyclic Metal Complexes, Springer, 2016.
[2] A. Facchin, M. Zerbetto, A. Gennaro, A. Vittadini, D. Forrer, C. Durante, ChemElectroChem 2021, 8, 2825–2835.
[3] A. Facchin, T. Kosmala, A. Gennaro, C. Durante, ChemElectroChem 2020, 7, 1431–1437.

OR087

Chitosan-based films as suitable multifunctional formulation in cosmetics and biomedicine

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Due to the pollution problem, the incoming use of novel sustainable materials for reducing the environmental impact is growing in different fields, particularly in cosmetics and biomedicine. For this purpose, our research was aimed to develop Chitosan-based films blended with Snail Slime as potential masks or functional patches, suitable for cosmetics and biomedical applications, respectively. A preliminary morphological, physical, and chemical characterization of these hybrid films was performed by attaining SEM, UV-Vis, ATR-FTIR and Water Vapor Transmission Rate measurements, evidencing a uniform distribution of the Snail mucus inside the Chitosan films, forming compacted and strongly cross-linked structures. XRD analyses demonstrated their amorphous nature. Furthermore, for assessing their stability in water medium, the swelling measurements were acquired when changing the pH, ionic strength, and temperature. The antioxidant features were investigated by means of the ABTS assay, and by monitoring the oxidation of a sulphur nucleoside, the 4-thiotymidine, a molecular probe for H_2O_2. The obtained results confirmed the findings. Work is in progress for testing in-vitro Chitosan-based blended films' antioxidant, as well as anti-inflammatory properties, with the aim also to assess their potential effect on improving wound healing, thanks to the Snail Slime components content. [1, 2] Furthermore, Chitosan/Snail Slime blended films' sunscreen, moisturizing, and skin-lightening properties will be explored, for making them suitable also as potential cosmetic multifunctional formulations. [3] In-vitro experiments for testing also the Chitosan/Snail Slime blended films' antimicrobial properties will be planned.

[1] J. Gubitosa, V. Rizzi, P. Fini, A. Laurenzana, G. Fibbi, C. Veiga-Villauriz, F. Fanelli, F. Fracassi, A. Onzo, G. Bianco, C. Gaeta, A. Guerrieri, P. Cosma, Soft Matter, 2020, 16, 10876
[2] A. Onzo, R. Pascale, M. A. Acquavia, P. Cosma, J. Gubitosa, C. Gaeta, P. Iannece, Y. Tsybin, V. Rizzi, A. Guerrieri, R. Ciriello, G. Bianco, Journal of Mass Spectrometry, 2021, 56:e4722.
[3] V. Rizzi, J. Gubitosa, P. Fini, S. Nuzzo, A. Agostiano, P. Cosma, Journal of Photochemistry & Photobiology, B: Biology, 2021, 224, 112309

OR088

The "end of life" of wastes becomes a new beginning: wastes as adsorbents for water decontamination and source of active molecules for the nanoparticle's green synthesis in biomedicine

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Each year around 20 % of food produced in the European Union (EU) is wasted get worsening social, environmental, and economic problems. For that reason, EU is trying to solve the problem incentivizing food wastes management for the developments of sustainable paths for innovative recycling approaches. So, the circular economy has become the focus of a recent major EU policy program. In particular, the EU Action Plan for the Circular Economy (European Commission, 2015) lists biomass and bio-based products as interesting resources (outputs) to be up-cycled to "new input products". On this ground, this work would meet the strategies of H2020 and Horizon-Europe, providing societal benefits in terms of improved health care and quality of life for a sustainable and inclusive growth of society preserving environment. Accordingly, multifunctional, low-cost, and environmentally friendly nanoparticles (NPs) for applications in nanomedicine and cosmetic will be developed, with the ambitious aim to scaling up the laboratory experience to industrial scale demonstrating the large production. [1,2] All the processes would respect the green chemistry and sustainability, with the aim to reduce the whole environmental impact by respecting the European Green Deal and the United Nations Sustainable Development Goals. Specifically, by adopting safe-by-design approaches, contributing towards the framework of EU nanosafety, the food and agricultural wastes, as olive and grape pomace, fruit peels, wasted vegetables and other typical food products of Italy, will be used as source of bioactive molecules for the green synthesis of NPs in water medium. The waste materials will be only washed with water extracting bioactive molecules needed for the synthesis preventing the use of toxic reagents. Moreover, to avoid the disposal of the solid wastes, derived from the pre-treatments with hot water (so, hard, and not safe conditions of work will be intrinsically avoided before their use), they would be proposed as recyclable long lasting adsorbents materials to remove emerging contaminants (for the first time) and textiles dyes from water. Mixture of pollutants will be also removed with high efficiencies, and the mechanism of adsorption will be detailed searching the best adsorbent (or more than one) to be used for real applications in presence of industrial effluents. [3,4] The recycling of both the adsorbent and the pollutants will be also attempted by green approaches.

[1] J . Gubitosa, V. Rizzi, A. Lopedota, A. Laurenzana, G. Fibbi, F. Fanelli, A. Petrella, V. Laquintana, N. Denora, R. Comparelli, P. Cosma, J. Colloid. Interf. SCI, 521 (2018) 50
[2] J. Gubitosa, V. Rizzi, P. Fini, R. Del Sole, A. Lopedota, V. Laquintana, N. Denora, A. Agostiano, P. Cosma, Mater. Sci. Eng, 106 (2020) 110170
[3] V. Rizzi, D. Lacalamita, J. Gubitosa, P. Fini, A. Petrella, R. Romita, A. Agostiano, J.A. Gabaldón, M. I. F.Gorbe, T. Gómez-Morte, P. Cosma, Sci. Total Environ., 693 (2019) 133620
[4] V. Rizzi, J. Gubitosa, R. Signorile, P. Fini, C. Cecone, A. Matencio, F. Trotta, P. Cosma, Chem. Eng. J., 411 (2021) 128514

OR089

Singular Spectrum Analysis as a signal/noise separation tool

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Noise is a constant presence in life and in all measurements. The role of noise is two-fold. It can be both a “nuisance” and a “resource”, when it is recognized as non-white, i.e. coloured, and therefore provides information on the processes that generate it. Analysis of noise is becoming significant in the study of chemical, physical and even physiological processes. Indeed, the presence of noise is intrinsic to the microscopic properties of matter. Its investigation has led to the development of new mathematical and analytical tools. In a series of data, or signal, be they function of time or of space, the components can be loosely divided into deterministic and noise-related that is stochastic. The deterministic component is usually further divided into a trend and oscillatory parts.
Singular Spectrum Analysis (SSA) is one of methods of choice to separate accurately noise from the other components of a signal. It is based on the Karhunen–Loeve transformation that ensures the decomposition into a set of orthogonal components. It is a non-parametric method that can be automated for signal denoising and gives the possibility to analyse the different signal components individually, in order to obtain information on all the processes that are present.

To date, SSA has not yet found great many applications in chemistry. Worth mentioning are the removal of solvent artefacts in multidimensional NMR of weak signals of proteins and the analysis of molecular dynamics of ionic liquids that was able to distinguish the different time scales of the ion diffusion and ultimately improved the phase-space plot for glass transition.

Here I will present results on the use of SSA as a denoising tool for the improvement of the Rietveld refinement of powder X-ray diffractograms and for the denoising of images from experiments of electrochemiluminescence, ECL. In the first case, SSA improves the goodness of fitting thereby allowing for faster scan speeds without loss of resolution in the diffractogram. In the second case, the study of the denoised images helped to obtain new insight into the ECL mechanism.

OR090

On-surface synthesis of boroxine-based molecules

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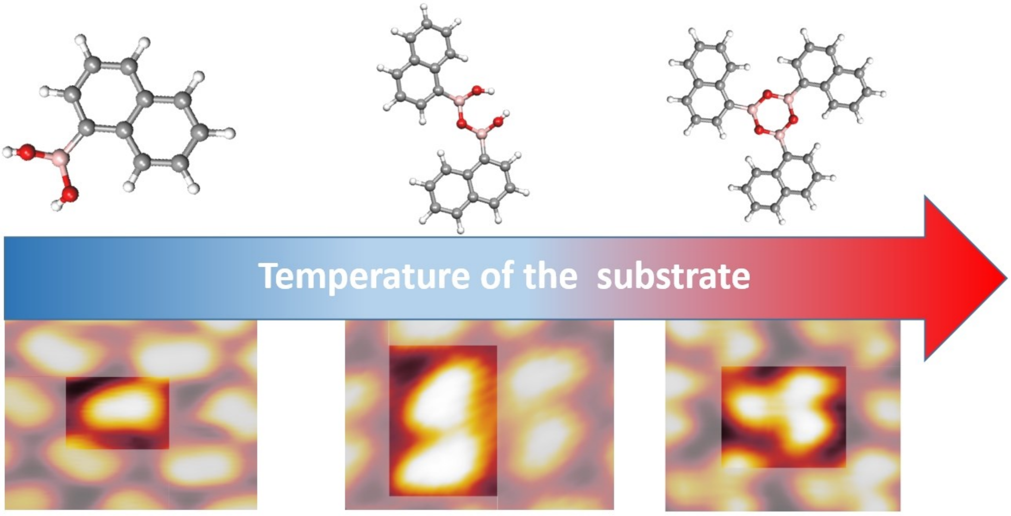

The boronic condensation is widely used for the synthesis of Covalent Organic Frameworks. We adopted it for the synthesis, on-surface and under Ultra High Vacuum, of large boroxine-based molecules (BBMs)[1,2]. By combining Scanning Tunneling Microscope (STM) imaging with X-ray spectroscopy, we characterized both the morphology and the electronic properties of ultra-thin films of BBMs grown on the Au(111) surface. The boroxine-Au(111) interaction drives the formation of a hybrid electronic orbital that exhibits ultra-fast charge transfer, making BBMs potentially of interest as charge mediators between the substrate and possible guest molecules deposited on top of the BBM-Au template. In this talk, I will in particular focus on the synthesis of the tri-naphtyl boroxine (TNB) as well as on the formation of larger molecular species obtained upon thermal treatment of the system. I will describe the electronic properties of the films at the different synthesis stages. A low temperature phase is isolated, where the boroxination process has only partially taken place, with the preliminary formation of dimers of naphtyl molecules. At higher temperatures, the synthesis of TNB is complete. At that stage, both photoemission and STM imaging suggest that thermal treatment of TNB film promotes the cleavage of a Boroxine-naphtyl bond, the desorption of a naphthyl group and the formation of a B-B bond between two adjacent bi-naphthyl boroxine fragments. (Figure adapted from [2])

[1] D. Toffoli et al., *Chem. Sci.*, 2017,8, 3789-3798
[2] E. Turco et al., *Chemistry* 2021, *3*(4), 1401-1410

OR091

Kesterite thin-films deposited by sol-gel techniques with tunable bandgap as absorbers for photovoltaic applications

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Currently, the PV research focuses on finding low cost and easily processable materials. Here, we propose a simple chemical procedure for synthesizing Earth-abundant chalcogenide thin-films with tunable bandgap, leading to well-defined phases of Cu_2XYS_4 (with X = Zn, Fe; Y = Sn, Ge). The deposition process is straightforward and very cheap, based on the sol-gel technique, where the thin films are produced thanks to a direct drop-casting of the precursor solution, followed by a gelation process and heat treatment in argon atmosphere to generate the desired crystalline phase of the quaternary alloy. Metal acetate precursors were proved to have a primary role in creating a network, during the sol-gel transition, by coordinating and pre-organizing the metals in solution, together with thiourea (as the only source of Sulphur) and DMSO as solvent. Moreover, the addition of dopant amounts of KCl into the precursor solution was experimentally demonstrated to be beneficial for the grain growth and material quality, both crucial for the final solar device performance. XRD, µ-Raman, UV-Vis, and EDX spectroscopy measurements have supported the characterization of the so-synthesized layers (CZTS, Fe-substituted CZTS, Ge-substituted CZTS); their morphology was studied by SEM imaging, confirming the thin-film good quality. The bandgap, obtained from transmittance measurements, ranges from 1.4 to 2.1 eV depending on the combination of the chosen metal precursors, suggesting this class of materials as a suitable candidate as a top absorber in a tandem device architecture and promising single-junction prototypes of working solar-devices have been produced, even on semi-transparent substrate. [1 - 4]

[1] V. Trifiletti et al. Chemistry Select 4 (2019) 4905.
[2] V. Trifiletti et al. Materials 13 (2020) 1471.
[3] G. Tseberlidis et al. Solar Energy 208 (2020) 532.
[4] G. Tseberlidis et al. Solar Energy 224 (2021) 134.

OR092

Application of a D-Optimal Design of Experiments to a photocatalytic pilot plant for environmental issues

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The presence of emerging pollutants in the environment is finally receiving the proper attention, due to the dangerous side-effects that arise and due to the lack of precise regulation of these biologically active compounds (pharmaceuticals and personal care products, PPCPs, the most concerning ones). The research on this topic doesn't just involve the detection of all the compounds that are input every day from multiple sources, but also comprehend their environmental fate and the investigation on processes for their degradation. Actual wastewater treatment plants are not able to deal with these micro-contaminants, thus, it's mandatory to find new water treatment technologies to efficiently counteract the spread of these new contaminants [1]. In this work, we selected a model of experimental design to take into account different kind of variables, both quantitative and qualitative, on a photocatalytic process using TiO_2-based photocatalysts for pollutants abatement.

The materials were tested on a pilot plant with volume of 1L set-up according to Figure 1: a reactor placed under magnetic stirring with an adjustable volume was connected to a peristaltic pump, whose flow was directed to a glass coil, placed under solar simulated irradiation lamps. The circuit was then closed by the flow reaching the mixing reactor. We decided to investigate the significance of 7 different variables: photocatalyst concentration, initial pH, treatment time, lamps positions, stirring rate, type of pollutants (dye) and type of photocatalysts. Being these variables of different nature (quantitative and qualitative), a D-Optimal design of experiment was chosen to extract the significance of each investigated variable, possible interactions among them and eventually the optimized conditions to carry out the photocatalytic process. In addition, investigated variables could be modified over different levels and considering their difference. As a conclusion, deduced information will lay the foundation for the industrial scale up that will allow the exploitation of photocatalysis as part of water treatment processes in order to try to solve the environmental issue caused by the presence of emerging pollutants.

This work was partially supported by the AMGA Foundation through the PROJECT 4.0 2020.

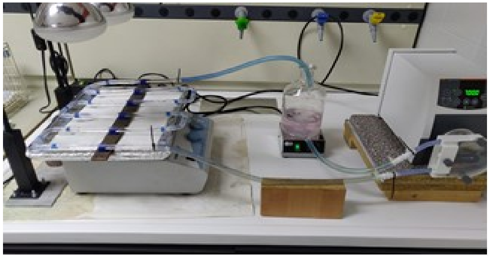

Figure 1: Photocatalytic pilot plant and its components: reactor, peristaltic pump and glass coil

[1] A critical review on application of photocatalysis for toxicity reduction of real wastewaters. J.J. Rueda-Marquez et al. / Journal of Cleaner Production 258 (2020) 120694.

OR093

Synthesis, Application, and Analytical Investigation of a TiO_2/PeL Coupled Photocatalyst for the Environmental Issue of Emerging Contaminants in Water

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The exploitation of heterogeneous photocatalysis as process intended for wastewater remediation is a topic which has been widely investigated during the last decades. The photoactivity of materials like TiO_2, triggered by irradiating with a proper wavelength, can generate reactive oxygen species, such as hydroxyl radical, that can easily react with organic molecules and lead to their degradation. For this reason, the use of TiO_2 for the treatment of waters and wastewater is promising towards the degradation of emerging organic pollutants that are affecting the quality of water, i.e., the pollution caused by the continuative replenishment into the environment of compounds deriving from pharmaceutical and personal care products [1]. As common wastewater treatment plants are not able to degrade the pollutants belonging to this class, scientific research has put much effort in order to find a suitable way to face this threat [2]. An innovative TiO_2-based catalyst for photo-oxidation processes was prepared in our laboratory. TiO_2 was synthesized via a sol-gel process and later coupled with a commercial persistent luminescence "PeL" material, in order to provide a support which is also able to act as internal irradiation source [3]. To find the best synthetic conditions leading to the most effective photocatalyst, a factorial experimental design (2^3) was applied, by investigating the degradation of methylene blue used as model pollutant and considering the MB abatement degree as response to be maximized. The optimized sample was then tested on the degradation of a real emerging pollutant, i.e., salbutamol; as it is not removed by classical wastewater treatments, it represents an appropriate case study to test the prepared photocatalyst. A photo-oxidation experiment was performed to investigate salbutamol degradation: a solution containing both salbutamol and the synthesized photocatalyst in water was subjected to simulated solar light irradiation and the analyte concentration was monitored over time. Several aliquots of the solution were sampled at constant time intervals and analyzed by means of UV-Vis spectrophotometry. Then, salbutamol degradation was confirmed by a highly specific HPLC-MS/MS method. The results showed a rapid decrease of the pharmaceutical concentration, which was completely depleted after 2 hours and an experiment performed in the same conditions, but without the photocatalyst, confirmed the effectiveness of the prepared material. A further confirmation of obtained results was achieved by means of Ionic Chromatography. Eventually, a study based on untargeted HPLC-MS analysis was carried out for the identification of degradation by-products.

[1] Krzeminski P., Tomei M.C., Karaolia P., Langenhoff A., Marisa C., Almeida R., Felis E., Gritten F., Andersen H.R., Fernandes T., Manaia C.M., Rizzo L. and Fatta-Kassinos D., Sci. Total Environ. (2019), 648, 1052-1081.
[2] Jianlong W. and Shizong W., J. Environ. Manage. (2016), 182, 620-640.
[3] Alberti S., Locardi F., Sturini M., Speltini A., Maraschi F., Costa G.A., Ferretti M. and Caratto V. J. Nanotechnol. Nanomedicine. (2018), 9, 3, 1-6.

OR094

Silica particles derived from natural Kaolinite for the removal of organic dyes from polluted water

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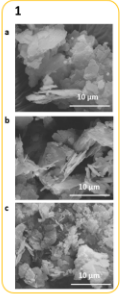
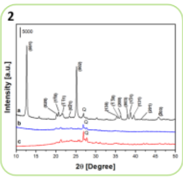
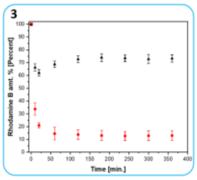
In the last decades, the quality of waterbodies suffered a sharp decline due to anthropogenic activities [1]. In particular, toxic dyes deserve growing attention due to their harmful effect on the ecosystem and human health [2]. To limit the continuous spreading of noxious species in the surrounding waterbodies, several methods can be employed [3]. In this respect, adsorption deserve particular attention due to its low costs, versatility and performances [4]. Among the most used sorbents, (*i.e*. silicas, zeolite and activated carbons [1,4]) natural clays are often used for the treatment of wastewaters thanks to their low cost, environmental sustainability and high natural abundance [5]. In this respect, this work deals with the thermal and chemical modification of a natural kaolinite that was calcined at 700 °C and treated with HCl to remove aluminum thus obtaining a siliceous material. The structural changes and the physico-chemical properties of the materials at different stages of thermal and chemical modification were investigated with several techniques including XRPD, MAS-NMR, SEM-EDX, FT-IR and N_2 physisorption at 77 K. The ability of parent kaolinite and siliceous material to capture the organic dye Rhodamine B from aqueous phase was investigated by means of UV-Vis spectroscopy. The siliceous material exhibited better adsorption capacity with respect to the parent kaolinite. Finally, the functional stability of the siliceous material was tested over three cycles of regeneration and adsorption.







[1] E. Boccaleri et al., Materials 2021, 14, 6196
[2] R.P. Schwarzenbach et al., Annu. Rev. Environ. Resour. 2010, 35, 109–136
[3] P.R. Gogate et al., Advances in Environmental Research 2004, 8, 553–597
[4] V. Miglio et al., Molecules 2021, 26, 1316
[5] F. Carniato et al., New J. Chem. 2020, 44, 9969–9980

OR095

Combining Simulations and Synchrotron Resonance Raman Experiments to explain the Selective Enhancement of Peptide Raman Signals

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Amide spectral signals dominate the spectroscopic response of proteins solvated in their natural environment, i.e., aqueous solution. Since N-acetylglycine-N-methylamide and N-acetylalanine-N-methylamide (also called NAGMA and NALMA, respectively) serve as prototypes for proteins,[1] in this work, we investigate their peculiar Ultraviolet Resonance Raman (UVRR) spectroscopic signatures using a combination of state-of-the-art experiments and simulations. UVRR spectra are recorded by tuning Synchrotron Radiation (SR) at several excitation wavelengths and modeled by using a recently developed multiscale protocol based on a polarizable QM/MM approach.[2]

Our results suggest that the selective enhancement of the amides signals is hydrogen bonding-induced because is intimately linked to the effect that water molecules exert on the C=O and N-H, C-N vibrations. We demonstrated that the inclusion of explicit water molecules concentrates the orbitals involved in the charge transfer in the C-N zones, which ultimately leads to the strong UVRR enhancement of vibrations that have large components of C-N stretching, particularly the AII signal. Thus, quantum effects must be present in any modeling of the solute-solvent interactions of RR spectroscopy for such systems. In addition, due to the constant movement of the solute and its surrounding water molecules, a single snapshot (or cluster composed of the solute and some surrounding water molecules) is not representative of the dynamical nature of the system, and can lead to a heavily biased results if taken to be representative for the ensemble, which is more correctly modelled through an explicit average over a large set of structures. [3]

Acknowledgements
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[1] B. Rossi, S. Catalini, C. Bottari, A. Gessini, and C. Masciovecchio, in UV and Higher Energy Photonics: From Materials to Applications 2019, edited by G. Lérondel, Y.-H. Cho, A. Taguchi, and S. Kawata, International Society for Optics and Photonics (SPIE, 2019), vol. 11086, pp. 23 – 32.
[2] S. Gómez, F. Egidi, A. Puglisi, T. Giovannini, B. Rossi, and C. Cappelli, Journal of Molecular Liquids 346, 117841 (2021).
[3] T. Giovannini, F. Egidi, and C. Cappelli, Chemical Society Reviews 49, 5664 (2020).

OR096

Molecular dynamics and the shades of noise

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Molecular dynamics can be described by the Langevin equation, where the effect of the random thermal collisions is represented by a noise term. Noise drives the dynamics and can positively improve the efficiency of a dynamical process, for example in stochastic resonances. Truly random noise is often referred to as "white" because, like the color white, it contains all frequency harmonics in approximately the same amount so that its spectrum is flat. Noise can be colored, with the colors related to time-correlation and power spectral properties. Colored noises display a power spectral density proportional to $1/f^{\beta}$ (power-law noises): for example, red/Brownian noise has $\beta=2$, pink noise has $\beta=1$, blue noise has $\beta=-1$ and violet noise has $\beta=-2$. An often-untold story is that the individual noise realizations (or values) can be drawn from different probability distributions, pdf. Colored noises drawn from diverse pdf's can be thought of as having a shade. In the majority of cases, thermal fluctuations usually stem from a Gaussian distribution, but other distributions can be considered. Indeed, the experimental improvement of spatial and temporal resolution has led to the observation of an ever-increasing number of non-Gaussian processes. The effect of different "shades" of noise in physico-chemical processes can be theoretically investigated by computer simulations. Recently, we showed by computer simulations, that noise, in the form of stochastic perturbation of particles interactions, can increase the efficiency of a chemical catalytic reaction.[1]

Here I will discuss the physical origin of different "shades" of white and colored noises and their effect on molecular dynamics. In particular, I will report on the dynamics of double minima systems, such as the inversion of the ammonia umbrella, the formation and disruption of hydrogen bonds, and the dynamics of rotating moieties. I will further address the relation of the pdf's and the timescales where dynamical effects appear. Ultimately, I will provide guidelines to detect experimentally the presence of different pdf's.

[1] F. Lugli, F. Zerbetto J. Phys. Chem. C 123 (2019) 825

OR097

Computational vibrational spectroscopy in generalized internal coordinates

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Spectroscopies, such as infrared and Raman, are powerful tools for the investigation of the physical chemical properties of molecular systems, providing detailed information related to their structure and dynamics. However, experimental spectra are tuned by several intertwined effects, which can make the interpretation of experimental data very challenging or even unfeasible without the support of reliable computational models. [1,2] Among the possible routes for the inclusion of anharmonic effects in the simulation of the vibrational spectra, the vibrational second-order perturbation theory (VPT2) [3-5] offers a good accuracy/cost ratio, giving the possibility to study also medium-to-large size systems. Generalization of the method to a flexible perturb-then-diagonalize (P2D) model (issuing from the so-called generalized (G)VPT2 model) further increases its accuracy. However, the customary framework of Cartesian-based normal coordinates is not able to describe correctly low-frequency, highly anharmonic, large amplitude motions (LAMs), due to the truncated polynomial approximation of the potential energy. A possible solution to this issue is the separation of the normal modes in order to isolate LAMs. With the target of simulating vibrational spectra of small- to medium-sized molecules presenting some flexibility soon, the first step is then the choice of a suitable set of internal coordinates, in order to decouple LAMs from the other modes as much as possible. In fact, Cartesian-based normal coordinates are ill-suited for this purpose. Then, small amplitude motions (SAMs) can be treated at the P2D level, while LAMs can be effectively described by low-dimension variational approaches. In order to reach this goal, the development of the P2D framework in terms of normal modes built from generalized internal coordinates is the first step. Based on the available literature, [6-8] the general expression of the vibrational Hamiltonian in internal coordinates has been derived, followed by the derivation of both energies and resonant terms, including the calculation of the variational correction required in the P2D method. Interestingly, all quantities of interest (such as energies and resonant terms) can be written as generalizations of the corresponding Cartesian-based expressions, making the overall implementation far more manageable. The reliability of the new methodology will be illustrated through selected test-cases.

[1] S. Stuart et al. Phys. Rev. B 60 (2009) 3320
[2] P. Morris et al. Phys. Rev. Lett. 70 (2008) 214
[1] V. Barone. Wiley Interdiscip. Rev. Comput. Mol. Sci. 6 (2016) 86
[2] C. Puzzarini et. al Chem. Rev. 119 (2019) 8131
[3] H. H. Nielsen Rev. Mod. Phys. 23 (1951) 90
[4] V. Barone J. Chem. Phys. 122 (2005) 014108
[5] M. Mendolicchio et. al J. Chem. Theory Comput. 17 (2021) 4332
[6] C. R. Quade J. Chem. Phys. 64 (1964) 2783
[7] A. D. Isaacson J. Chem. Phys. A 110 (2006) 379
[8] B. Podolsky Phys. Rev. 32 (1938) 812

OR098

Structure and stability of thiol monolayers on gold through MD simulations, GIXRF and XPS measures

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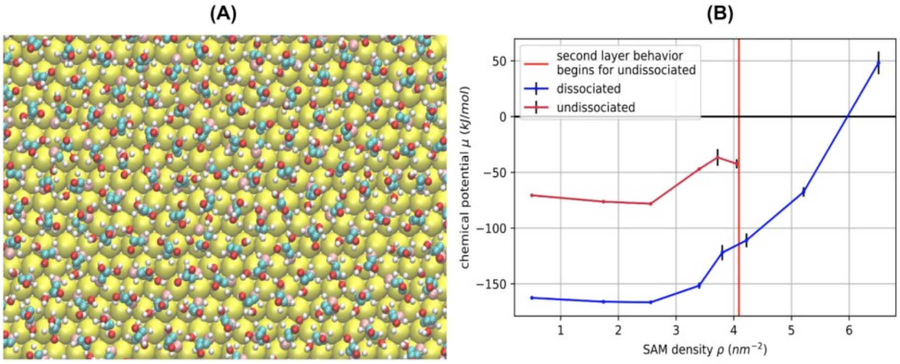
Self-assembled monolayers (SAM) of thiol molecules on gold surfaces are of central interest in surface science; they are studied for potential applications, among others, in nanolithography, biosensing, and electronics [1]. The nature of the sulfur/gold interface is still debated: although it is commonly held that the –SH moiety dissociates to form a covalent S-Au bond, several studies report SAMs of undissociated thiols [2,3].

To get insights on this point, we combined density functional theory (DFT) and molecular dynamics (MD) simulations to study in detail the thermodynamics of SAM formation on gold surfaces, using 7-mercapto-4-methylcoumarin (MMC) and 3-mercaptopropionic acid (MPA) as model molecules. The chemical potential of a thiol molecule in the SAM was computed by MD thermodynamic integration as a function of the SAM density; the maximum SAM densities for MMC and MPA in dissociated and undissociated form were computed and compared with experimental results.

The experimental SAM densities were measured through reference-free grazing incidence X-ray fluorescence (GIXRF), and the nature of the chemical bond was investigated with X-ray photoelectron spectroscopy (XPS). The computational values obtained for the expected SAM densities were (nm^{-2}): $MMC_{dissociated}$=4.0, $MMC_{undissociated}$=3.7; and $MPA_{dissociated}$=6.0, $MPA_{undissociated}$=4.1. These values are to be compared with the experimental results of (nm^{-2}) MMC_{exp}=4.6±0.6, MPA_{exp}=7.6±1.1.



(A) Top view of an equilibrated SAM of MPA from a MD trajectory. **(B)** Chemical potential for MPA as a function of SAM density.

[1] *Chem.Soc.Rev.*, 2010, 39, 1805–1834.
[2] *Phys. Chem. B,* 2005, 109, 33, 15992–15996.
[3] *Nat. Chem.,* 2019, 11**,** 351–358.

Au nanostars for labeling nanoplastics on real alumina filters

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Microplastics pollution is recognized as a global concern in air, terrestrial, but most of all in aqueous environments.[1] These materials are intrinsically heterogeneous in dimensions and polymers, so that standardized analytical methodologies for their complete characterization are still missing. Among other instrumental techniques, µ-FTIR and µ-Raman had recently attracted attention due to the possibility of providing both morphological and chemical characterization. Because of visible excitation wavelengths are used, µ-Raman allows superior spatial resolution in respect of µFTIR. For this reason, it represents the most promising technique for the smallest microplastics fraction, called nanoplastics. However, nanoplastics are difficult to find by optical microscopy and Raman measures usually require long acquisition time. An innovative methodology to address nanoplastics detection in alumina filters, routinely adopted for real environmental samples,[1] is herein presented. Inspired by the principles of cell labelling,[2] gold nanostars (AuNS) are functionalized in order to act as SERS-tags and selectively couple to 800 nm polystyrene beads (PS). The intrinsic bright signals provided by the AuNS are therefore used to run a quick survey of the filter surface. [3,4] Only the areas resulting with the characteristic SERS signals of AuNS will be also mapped at higher resolution. This allows to detect both AuNS and PS signals. The results of this study promise to shorter the overall measuring time of microplastics achieved by µ-Raman.

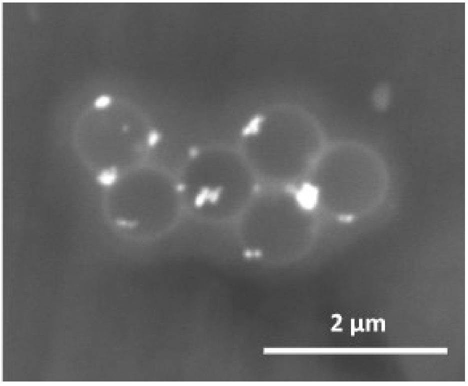

Figure 1: SEM image of PS nanoplastics labelled with AuNS (the brighter spots).

[1] Martelloni at al. Rapporti ISTISAN 21/2 (2021)
[2] L. Litti et al. Sci. Rep. 10 (2020) 15805
[3] L. Litti et al. ACS Appl. Mater. Interfaces 13 (2021) 34752
[4] L. Litti et al. Nanoscale Horiz. 5 (2020) 102

Multi-site porous catalysts for single-reactor tandem processes

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Functionalizing bio-based furanic derivatives in a minimum number of synthetic steps is of huge interest to increase the molecular diversity and complexity. It would be desirable to devise simple, easily accessible, and robust catalysts affording multi-step reactions to engineer intensified processes and avoiding the separation of intermediates. One-pot reactions have been developed targeting the synthesis of branched alkanes as jet fuels and monomers for polyester and epoxy resins starting from the aldol condensation of furfural (FF) with ketones, followed by hydrogenation. The reaction is catalysed both by acid or basic sites and alkaline metal oxides or zeolites and metal-substituted zeotypes can be used as catalysts. Acid or base catalysts can be also combined with metal nanoparticles (*e.g.*, Pd) to engineer aldol condensation-hydrodeoxygenation/hydrogenation tandem reactions.

In this contribution, the optimization of two multi-site porous catalysts for single-reactor tandem aldol condensation of FF with methylisobutylketone (MIBK) followed by hydrogenation is presented. Pd nanoparticles were deposited by in situ reduction procedure on hierarchical zeo-type materials containing Brønsted acid sites [1] and on organic-inorganic hybrid systems containing accessible pendant amine groups as basic sites.[2] A series of crystalline silicoaluminophosphate SAPO-5 catalyst with hierarchical porosity, to ensure better mass transport and acid sites accessibility, and variable silicon content were synthesized by a bottom-up method and tested over the aldol condensation reaction between FF and MIBK. The best performing one was further functionalized with Pd to obtain the bifunctional catalyst. Similarly, a series of organic-inorganic hybrid bifunctional organosiliceous catalysts with accessible pendant amine groups as single basic sites and Pd nanoparticles was prepared from suitable synthesis processes. Structural, textural properties and acid strength and accessibility of hierarchical SAPO-5 and basic sites accessibility of hybrid organosiliceous catalysts were monitored by using XRD, volumetric analysis and coupling ssNMR with FTIR spectroscopy of adsorbed probe molecules, both before and after the deposition of Pd nanoparticles. The two classes of bifunctional catalysts were successfully tested in the synthesis of hydrogenated furan- and THF derivatives in the one-reactor tandem aldol condensation/crotonization reaction between FF and MIBK, followed by hydrogenation with molecular hydrogen.

[1] L. Gao et al. J.Catal. 397 (2021) 75
[2] M. C. Hernández-Soto, et al. submitted to *Appl. Catal. B* (2022)

OR101

Modeling Nanoplasmonics: an Atomistic, yet Classical, Approach

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Most properties of plasmonic nanostructures follow from the tunability of their optical response as a function of their shape and dimensions [1]. Such a feature is typical not only of metal nanoparticles but also graphene-based nanostructures, for which an additional tunability, based on electrical gating, can be exploited. The accurate description of the optical properties of the plasmonic substrates is crucial for a theoretical understanding of the physical phenomena occurring at the plasmon resonance frequency [2]. Here, we present an atomistic, yet classical, approach to predict the plasmonic properties of nanostructures of complex shapes. Our approach is general enough to describe, at the same level of accuracy, metal nanoparticles [3,4] and graphene-based nanoaggregates [5], being able to correctly reproduce experimental trends.

Our classical approach show a remarkable potential for large scale nanoplasmonic simulations. In particular, by properly accounting for the atomistic discretization of matter, we can accurately describe the nanoplasmonics of systems dominated by quantum effects, such as subnanometer junctions [3,6] or by geometrical defects. In the selected test cases we will show how to engineer matter at the nanoscale to create very localized hot-spots, with potential application to single molecule detection [6,7].

[1] V. Giannini, et al. Chem Rev. 111 (2011) 3888
[2] J. Langer, et al. ACS Nano 14 (2019) 28
[3] T. Giovannini, et al. Nanoscale 11 (2019) 6004
[4] L. Bonatti, et al. Front. Chem. 8 (2020) 340
[5] T. Giovannini, et al. J. Phys. Chem. Lett. 11 (2020) 7595
[6] T. Giovannini, et al. in preparation
[7] L. Bonatti, L., et al. Nanoscale Adv. (2022) DOI: 10.1039/D2NA00088A

OR102

Visible light sensitized TiO_2 photoanodes for solar water splitting: coupling with Molybdenum doped $BiVO_4$

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Capturing and storing solar energy into hydrogen as clean fuel is a promising route to replace fossil fuels towards the development of a sustainable society. Photoelectrochemical (PEC) water splitting occurring at the semiconductor/electrolyte interface of both a photoanode and a photocathode in a tandem cell has emerged as effective strategy to this aim [1]. Identifying semiconducting materials acting as photoanodes for oxygen evolution with high efficiency and long-term stability is the major performance bottleneck of this device. TiO_2 is by far the most studied semiconducting metal oxide thanks to its remarkable stability and suitable band edge location towards both the anodic and cathodic semireactions. However, its relatively wide band gap of 3.2 eV strongly limits the exploitation of a large part of the solar light spectrum [2]. Coupling TiO_2 with a narrow band gap metal oxide, such as $BiVO_4$, would address this issue allowing for TiO_2 sensitization to visible light [3]. In this work, we propose a successful strategy to overcome the limits imposed by the unfavorable type I band alignment predicted at the interface of the two semiconductors in the $TiO_2/BiVO_4$ heterojunction, hampering the efficient separation of photogenerated electron-hole couples. A *hot electrons injection* mechanism from $BiVO_4$ to TiO_2 under visible light excitation, active only at $\lambda \leq 490$ nm, *i.e.*, for incident photons with an excess energy with respect to the $BiVO_4$ band gap, was indeed found at the basis of its unexpected functionality [3]. The coupled system outperformed only with respect to the UV-absorber oxide, not to the pure $BiVO_4$ system (Figure 1).

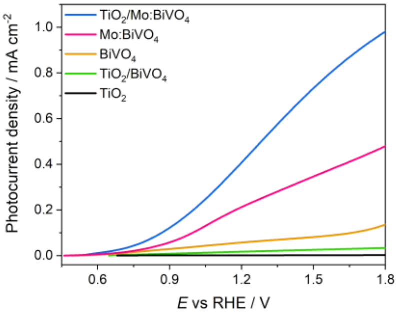

*Figure SEQ Figure * ARABIC 1. LSV plots in 0.5 M Na_2SO_4 electrolyte under irradiation with $\lambda \geq 400$ nm through the electrode/electrolyte interface.*

Differently, coupling TiO_2 with optimized molybdenum doped $BiVO_4$ determined a dramatic photoactivity increase of the resultant TiO_2/Mo:$BiVO_4$ heterojunction system with respect to both the undoped $TiO_2/BiVO_4$ composite material and each of the two single components (Figure 1). This impressive result can be explained by considering the establishment in the novel system of a staggered (type II) band edge alignment at the oxides interface. In particular, structural distortions of the $BiVO_4$ crystal structure [4] upon Mo^{6+} incorporation in the material bulk would play a key role for obtaining such band edges alignment, which may promote a beneficial visible light-induced charge carriers separation within the here investigated home-made heterojunction photoanodes.

[1] M. Grätzel Nature 414 (2001) 338
[2] M. V. Dozzi et al. Phys. Chem. Chem. Phys. 13 (2011) 18217
[3] A. Polo et al. Catal. Today 340 (2020) 19
[4] G. Di Liberto et al. J. Phys. Condens. Matter 33 (2021) 075001

OR103

New lead-free perovskite: synthesis and characterization of Mg-based solar cells

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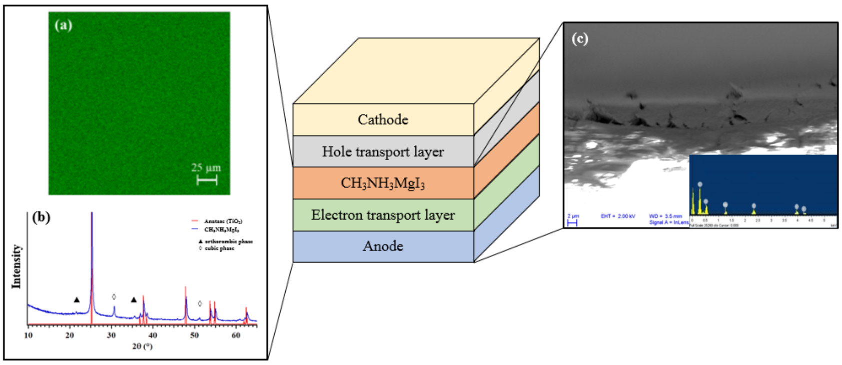
In the present work we realized a non-toxic lead-free perovskite solar cell (PSC) with low environmental impact. Perovskites are organic-inorganic materials with a ABX_3 structure (where A = monovalent organic cation, B = divalent metal, and X = halide) suitable for various fields of application such as solar cells, light emitting diodes and sensors due to their strong light absorption, band gap, excitation lifetime and dielectric properties [1].

The chemical composition of the new PSC active layer was chosen according to DFT/LDA calculations [2] substituting the more commonly used lead with magnesium to obtain a $CH_3NH_3MgI_3$ perovskite structure. The construction of the PSC device was realized in a multistep process: deposition of the electron transport layer, synthesis of the perovskite active layer, deposition of the hole transport layer and of the counter electrode. The synthesis of the photoactive layer was optimized changing the relative volume of the precursor (40 µL – 80 µL) and the annealing temperature (20 °C < T < 80°C). The XRD characterization of the Mg-PSC active layer confirms the presence of the perovskite structure, the morphology of the active layer obtained both from SEM/EDX and CLSM images shows the presence of a uniform distribution of the perovskite layer and confirming the chemical composition.

The photophysical characterization allowed to evaluate the properties of photoluminescence and the band gap of the device as a function of the preparation procedure. The efficiency and stability of the solar cells were estimated from I-V curves as a function of irradiation and storage time.



Schematic representation of the architecture of the Mg-perovskite. (a) CLSM image and (b) XRD pattern of the photoactive layer, (c) SEM and EDX of the device cross section.

[1] N. F. Atta et al. Perovskite Materials-Synthesis, Characterization, Properties, and Applications, 2016, Chap 4, IntechOpen, London, United Kingdom
[2] M. R. Filip et al. J. Phys. Chem. 120 (2016) 166

OR105

Nanomaterials for solar energy conversion and storage

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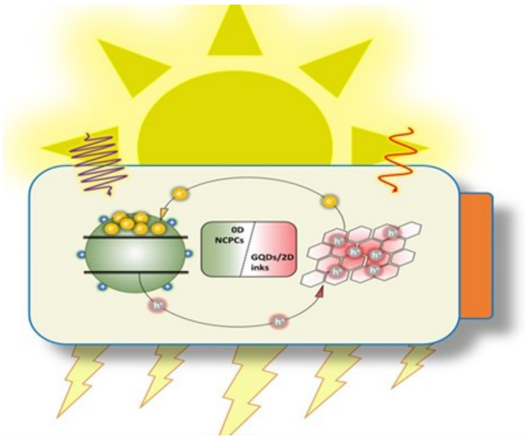
Electricity from solar power is the most promising alternative solution for the global sustainable energy supply. Nevertheless, an efficient exploitation of the sunlight is still a major challenge considering the fluctuations related to its intermittent availability. In this context, an efficient energy storage became a crucial turning point. Current photovoltaic technology relies on the use of separated systems for the energy storage, but this implies energy losses associated with the compartmentalization of the two devices. We can propose a disruptive innovation in solar technology with the idea of combining both technologies into one single unit by exploring a novel nanomaterial-based system that is capable of both, light energy conversion and storage. The cooperative electronic properties of a library of nanomaterials such as metal oxides, transparent conducting oxide nanocrystals, chalcogenides, and carbides etc. can be leveraged here with the concept of photodoping. Photodoping is one of the most interesting strategies for electronic doping of semiconductor nanomaterials. This photo-induced n-type doping offers a convenient way in-situ and non-destructively modify carrier densities in nanocrystals. The loss of the photoexcited hole in the photodoping process, which is sacrificed by reacting with the hole scavengers in solution is a prime concern in contemporary photodoping approaches. Replacing sacrificial hole scavengers with suitable hole collectors help to envisage a fully functional system that can completely participate in the charge storage processes. The development of new composite structures envisages a long-term impact on scientific and industrial scene both towards the large-scale exploitation of solar chargeable electrolytes for their use in flow cell batteries as well as for the realization of lightweight, miniature devices.



[1] M Ghini et al Nanoscale, 2021, 13, 8773– 8783
[2] I.Kriegel et al J. Phys. Chem. C 2020, 124, 8000−8007

Swellable Organic Modified Silica for the Removal of Pollutants from Aqueous Phases

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In recent years, the removal of chemical contaminants from water continues to be a central issue in environmental remediation. Chemical industries have focused on sustainable development approaches, promoting materials that offer performance at lower cost and significantly reducing environmental impact. Silica-based mesoporous materials have been synthesized and extensively studied for various applications, as they possess attractive characteristics such as high specific surface area, large pore size, and chemical inertness[1]. A promising innovative sol-gel-derived organosilica material for pollutant adsorption is represented by Swellable Organic Modified Silica (SOMS), whose structure allows for an expansion of three to five times its volume in the presence of organic compounds, thus enabling their adsorption[2]. SOMS silicas do not expand in water, making it a useful absorbent for wastewater treatment because volume increase occurs only when organic molecules are absorbed[3]. SOMS are synthesized by polycondensation of bis-(trimethoxysilylethyl) benzene using tetrabutylammonium fluoride as a catalyst. The methoxysilane groups react to form Si-O-Si bonds forming a network with bridging aryl groups to produce a porous and mechanically flexible matrix. Subsequently, to achieve swelling, the residual silanols on the surface are chemically modified with a chlorosilane to prevent condensation reactions during gel drying. In this work, SOMS silicas were synthesized and then tested as an adsorbent of organic pollutants from the aqueous phase. The physico-chemical properties of SOMS were determined using various experimental techniques. The ability of silica to remove a model organic pollutant (Rhodamine B) from an aqueous solution was evaluated by UV-Vis spectroscopy [4]. Adsorption tests were performed, both using the powder as it is, and after swelling with different organic solvents (acetone, acetonitrile and ethanol). The reference material is able to remove 42% of Rhodamine B after 24 hours of contact, while SOMS swelled with Acetone, Ethanol, or Acetonitrile is able to remove 100% of the pollutant concentration in solution (**Figure 1**). Specifically, after only 15 minutes of contact there is a removal of Rhodamine B concentration of 64% for SOMS swelled with acetonitrile, 70% for SOMS swelled with ethanol, and 98% for SOMS swelled with acetone. The adsorption of hybrid materials will be compared with that of different mesoporous silicas (i.e. MCM-41, SBA-15 and silica monoliths).

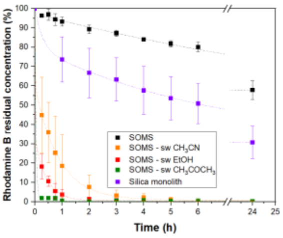

Figure 1. Concentration (%) decrease over time of $1.5x10^{-2}$ mM Rhodamine B water solution in the presence of Silica monolith (🟪), SOMS (■), SOMS swelled with Acetonitrile (🟧), SOMS swelled with Ethanol (🟥) and SOMS swelled with Acetone (🟩). Error bars represent standard deviations calculated on averaging results collected from three replicated experiments.

[1] P. N. E. Diagboya et al. *Microporous and Mesoporous Materials*, vol. 266, pagg. 252–267, 2018
[2] C. M. Burkett e P. L. Edmiston, *Journal of Non-Crystalline Solids*, vol. 351, n. 40–42, pagg. 3174–3178, 2005
[3] P. L. Edmiston e L. A. Underwood, *Separation and Purification Technology*, vol. 66, n. 3, pagg. 532–540, 2009
[4] S. Rasalingam, et al., *Applied Catalysis B: Environmental*, vol. 174–175, pagg. 49–59, 2015

Application of ATR-FTIR spectroscopy to study bacterial cell responses to the toxic selenite and tellurite oxyanions

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Fourier Transform Infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR) is a highly versatile, non-destructive, and label-free technique easily performable on both solid and liquid complex matrices or systems [1-2]. ATR-FTIR spectroscopy finds applications in several fields, including material science, analytical chemistry, pharmacology, forensics, cultural heritage, quality control, plant science, risk assessment, and biomedicine [3-5]. This spectroscopic technique has also recently gained scientific interest as a rapid and accurate tool for examining biological systems and their components under different conditions [1-2,6].

In the present study, ATR-FTIR spectroscopy has been performed to usefully delineate the physio-metabolic profiles of two Gram-positive bacteria strains (i.e., *Micrococcus* sp. and *Micromonospora* sp.) previously isolated from metal- and metalloid-rich Japanese wallpapers [7], upon their exposure to the toxic and common water pollutants selenite (SeO_3^{2-}) [8] and tellurite (TeO_3^{2-}) oxyanions. The obtained spectra highlight the involvement and modification, to various degrees, of proteins, lipids, polysaccharides, and thiol-containing or deriving molecules in response to the toxicity exerted by these oxyanions. A deep analysis of IR contributions suggests putative mechanisms and processes occurring within bacterial cells to decrease SeO_3^{2-} or TeO_3^{2-} toxicity. Although *Micrococcus* sp. and *Micromonospora* sp. cells exposed to SeO_3^{2-} or TeO_3^{2-} respectively showed some spectral similarities, ATR-FTIR spectroscopy underlines crucial differences that can trace back to both the diversity of oxyanions and the uniqueness of the chosen bacterial strains. Finally, univariate (i.e., Student's t-tests) and multivariate (i.e., Principal Component Analysis) statistical analyses have been applied to support and validate the statistical significance of the obtained results.

[1] V. Ricciardi et al. Appl. Sci. 10 (2020), 2974.
[2] S.E. Glassford et al. Biochim. Biophys. Acta - Proteins Proteom. 1834 (2013), 2849-2858.
[3] S. G. Kazarian et al. Analyst. 138 (2013), 1940-1951.
[4] M. M. Blum et al. Drug Test. Anal. 4 (2012), 298-302.
[5] G. L. Liu et al. Analyst. (2022), doi: 10.1039/d2an00005a
[6] S. G. Kazarian et al. Biochim. Biophys. Acta Biomembr. 1758 (2006), 858-867.
[7] E. Piacenza et al. Sci Rep. 10 (2020), 16072.
[8] E. Piacenza et al. Nanomaterials. 11 (2021), 1195.

OR108

Molybdenum doped $CuWO_4$-based heterojunction photoanodes for solar energy conversion

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$CuWO_4$ (band gap = 2.3 eV) has recently gained increasing interest in water oxidation, as a much better visible light absorber and more stable oxide alternative to WO_3 [1]. However, an efficient use of $CuWO_4$ as photoanode material requires to overcome its severe internal charge recombination, as ascertained in our recent photoelectrochemical (PEC) investigation on this material coupled with ultrafast transient absorption analysis [2].

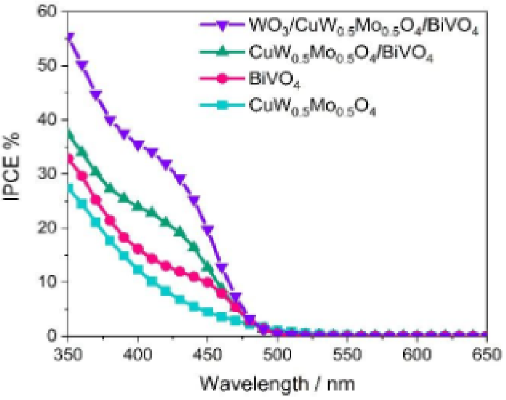

*Figure SEQ Figure * ARABIC 1. Incident photon to current efficiency (IPCE) of different photoanodes at 1.23 V vs. RHE, in 0.1 M K_3BO_3 electrolyte solution under front-side irradiation.*

In this work, this crucial issue of $CuWO_4$ photoanodes is addressed by adopting a partial Mo^{6+} for W^{6+} substitution strategy resulting in $CuW_{1-x}Mo_xO_4$ electrodes with a greatly enhanced visible light-induced photoactivity compared to pure $CuWO_4$. We thus systematically optimized both the film thickness in the wide 250-700 nm range and the Mo^{6+} for W^{6+} substitution degree (10-80%), by adopting an aqueous-based deposition procedure onto fluorine-doped tin oxide (FTO) glass substrates. A thorough PEC investigation under simulated solar light irradiation, either in pure water oxidation or in the presence of $NaNO_2$ as suitable electron donor species [3], led to the identification of the *ca.* 250 nm thick $CuW_{0.5}Mo_{0.5}O_4$ film with a 1:1 W:Mo molar ratio as the best performing electrode, ensuring an optimized compromise between light absorption and photogenerated charge carriers separation.

Furthermore, with the aim to further boost the charge carrier separation within the photoanodes, the best performing $CuW_{0.5}Mo_{0.5}O_4$ films were combined either in a heterojunction with $BiVO_4$ or in a double heterojunction with both WO_3 and $BiVO_4$. Incident photon to current efficiency (IPCE) analyses at 1.23 V vs. RHE demonstrated the definitely superior performance of both $CuW_{0.5}Mo_{0.5}O_4/BiVO_4$ and $WO_3/CuW_{0.5}Mo_{0.5}O_4/BiVO_4$ coupled systems compared to the individual components, over the entire investigated spectral range (Figure 1).

In particular, the photoactivity was found to be maximized under selective excitation of a sufficiently thick $BiVO_4$ overlayer, allowing to minimize the competitive electron-hole recombination path occurring instead under simultaneous excitation of the three oxides by irradiation through the FTO back-side.

[1] J. E. Yourey et al. J. Mater. Chem. 21 (2011) 7651
[2] I. Grigioni et al. J. Phys. Chem. C 125 (2021) 5692
[3] A. Polo et al. ACS Appl. Energy Mater. 3 (2020) 6956

OR109

Influence of Sulfur-Curing Conditions on the Dynamics and Crosslinking of Rubber Networks: A Time-Domain NMR Study

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Elastomers are polymeric materials extensively used for manufacturing a wide range of products for industrial applications, especially in the tire industry. These materials are obtained by vulcanization of one (or more) polydiene polymer(s) in the presence of sulfur and other additives (accelerators, activators, plasticizers, reinforcing fillers, etc.). During this process, chemical crosslinks are formed between the polymeric chains, which provide elasticity and durability to the final product. Furthermore, depending on the formulation and the vulcanization conditions, other mechanical properties required for industrial applications can be obtained. Importantly, such macroscopic properties are strongly related to the microscopic structure of the polymeric network [1]. Consequently, the investigation of microscopic and macroscopic properties giving access to information on the network structure in relation to the vulcanization conditions is fundamental for the optimization of processing and performance of elastomeric materials.

In this context, ^{1}H time-domain NMR (TD-NMR) represents a valuable tool to gain insights into the molecular dynamics of the polymeric chains. In fact, this technique allows to measure NMR observables (^{1}H T_1 and T_2 relaxation times and ^{1}H-^{1}H residual dipolar couplings (D_{res})), which depend on the modulation of ^{1}H-^{1}H dipolar couplings by segmental motions. These motions are quite fast in elastomers above glass transition temperature, but are anisotropic, resulting in residual ^{1}H-^{1}H dipolar interactions, which depend on the amount and distribution of topological constraints in the polymeric network [2].

In this work, natural and isoprene rubbers vulcanized at different curing temperatures and different sulfur contents have been investigated by exploiting ^{1}H TD-NMR techniques, including ^{1}H multiple-quantum experiments for the measurements of D_{res}, Carr–Purcell–Meiboom–Gill pulse sequence for the evaluation of ^{1}H T_2 relaxation times, and field cycling NMR relaxometry for the measurements of T_1 relaxation times on a wide range of Larmor frequencies (10 kHz-35 MHz). The NMR observables were compared with the crosslink density or macroscopic properties of the material that depend on this quantity, obtained using routinely employed methods in industrial analyses, allowing to gain insight into the effects of the formulation and the vulcanization conditions on the structure and dynamics of the polymeric networks [3].

[1] S. P. O. Danielsen et al., Chem. Rev. 121 (2021) 5092
[2] K. Saalwächter, Rubber Chem. Technol. 85 (2012) 350
[3] F. Nardelli et al., Polymers 14 (2022) 767

OR110

Crystal chemistry and thermodynamics of Cu_3As: the actual structure and physical properties

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Cu_3As, or domeykite, is the main Cu-As intermetallic commercially produced; it is mainly used in semiconductors and photo optic applications. Both a low- and a high-temperature phase are known.

Previous research reports Cu_3As to crystallize in the hexagonal anti-HoH_3-type structure (also anti-LaF_3-type), with Pearson's symbol *hP*24 and space group *P*–3*c* (No. 165). Only in one work the Cu_3As compound was reported to adopt the cubic Cu_3As prototype [*cI*64, *I*–43*d*, (No. 220)]. While in the latter case, analyses were carried out on a single crystal of a sample of the mineral domeykite, all other studies were performed on molten and high-temperature annealed samples of Cu_3As.

In our recent study, we synthetized the Cu_3As compound through heating stoichiometric samples at low and high temperatures (*i.e.*: 350, 400, 500 and 650°C) and investigated its crystal structure by X-ray diffraction (XRD) carried out both on single crystal and powder (Rietveld analysis). The data revealed the actual crystal structure of Cu_3As to be the hexagonal Cu_3P-type [*hP*24, *P*6_3*cm* (No. 185)] for both the low and high temperature forms of Cu_3As (Fig. 1). These results together with the physical properties and thermodynamic stability of this compound will be presented in this communication.

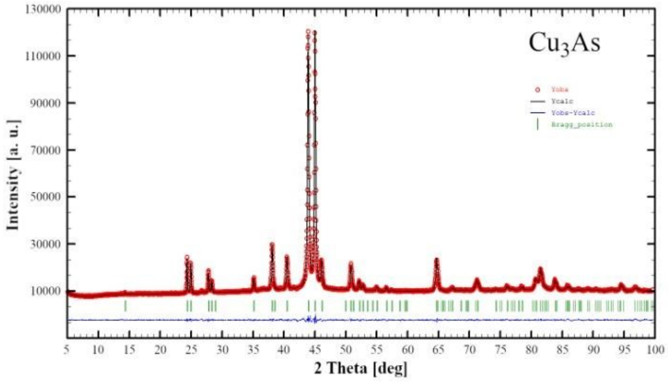

Fig. 1. Rietveld refinement profile on the X-ray powder pattern of a Cu_3As sample annealed at 400°C. The sample is single phase containing the Cu_3P-type Cu_3As compound.

[1] P. R. Subramanian, D. E. Laughlin, in: Subramanian P. R. (ed). *Phase diagrams of binary copper alloys*, ASM International, Materials Park, Ohio, USA, 1994, 43–52.

[2] P. Villars, K. Cenzual, *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, Release 2019/20, ASM International, Materials Park, Ohio, USA

OR111

Solid State NMR of Lead Halide Perovskites: unveiling structural complexity of 2D Ruddlesden-Popper phases

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In the fast-developing research of improved and sustainable materials for optoelectronics, 2D Lead Halide Perovskites (LHP) have attracted considerable attention because they offer the possibility of tunable band gap and enhanced environmental stability with respect to the corresponding 3D perovskites. 2D Ruddlesden–Popper (RP) perovskites can be prepared by adding a large organic mono ammonium cation, L^+, in the precursor solution. In this way the 3D structure of corner-sharing octahedra (ABX_3) is disrupted and a structure with a bilayer of spacer cations between metal halide sheets is formed ($L_2A_{n-1}B_nX_{3n+1}$). For example, butylammonium (BA^+) is a suitable organic cation to force the archetypical perovskite $MAPbI_3$ into 2D RP perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ (Figure 1), which are the object of the present study. The layer thickness of metal halide sheets is specified by n and can be adjusted by tuning precursor stoichiometry.

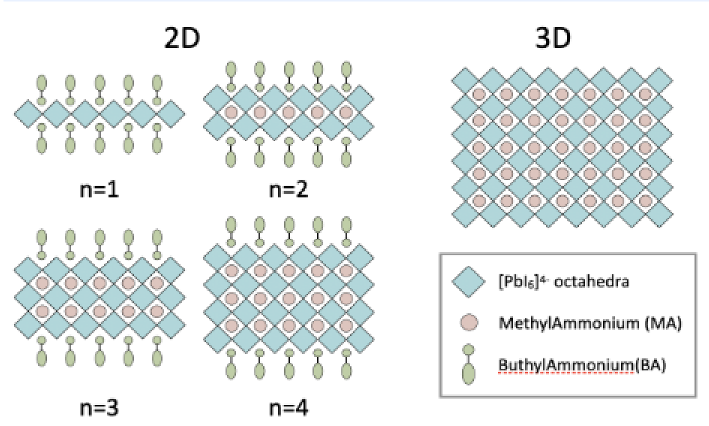

Figure SEQ Figura * ARABIC 1. Schematic structure of 2D RP perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ for n=1-4, and of the corresponding 3D perovskites $MAPbI_3$.

Solid-State NMR stands out as characterization technique for LHP for its ability to study ion dynamics, compositional variations and ion incorporation, chemical interactions, and degradation mechanisms [1,3]. In this work, the 2D RP perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ with n=1-4 have been characterized by ^{207}Pb, ^{1}H, and ^{13}C Solid-State NMR, both under Magic Angle Spinning and static conditions. The structural features of these systems have been compared with those of 3D $MAPbI_3$ and discussed in relation to very recent literature [3].

[1] W. M. J. Franssen, A. P. M. Kentgens, *Solid State Nucl. Magn. Reson.*, 100 (2019) 36-44
[2] L. Piveteau, V. Morad, M. V. Kovalenko, *J. Am. Chem. Soc. 142* (2020) 19413-19437
[3] D. J. Kubicki, S. D. Stranks, C. P. Grey, L. Emsley *Nat Rev Chem* 5 (2021) 624–645
[4] J. Lee, W. Lee, K. Kang, T. Lee, S. K. Lee, *Chem. Mater.*, *33* (2021) 370-377

OR112

Spin Density Topology

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Despite its role in spin density functional theory and it being the basic observable for describing and understanding magnetic phenomena, few studies have appeared on the electron spin density subtleties thus far. In contrast to the plethora of studies on topological features of other scalar fields of chemical interest [1,2], a full topological analysis of the spin density was still lacking until the first paper on the topic was published by our group in 2020 [3]. The developed theory of spin density topology allows to unveil the kind of information hidden in the spin density distribution that only its topology can disclose. Herein, we address the significance of the spin density critical points, the 18 different ways in which they can be realized and the peculiar topological constraints on their number and kind, arising from the presence of positive and negative spin density regions. Besides, we introduce the notion of molecular spin graphs, spin maxima (minima) joining paths, spin basins and their *valence*. We show that two kinds of structures are associated with a spin–polarized molecule: the usual one, defined through the electron density gradient, and the *magnetic* structure, defined through the spin density gradient and composed in general by at least two independent spin graphs, related to spin density maxima and minima (Figure 1). We also define several topological descriptors, such as the spin polarization index, which enable to characterize the properties of spin density critical points and basins. The theory is then applied to the exemplary case of the water molecule in the $^3B_1$ triplet state, using spin density distributions of increasing accuracy.

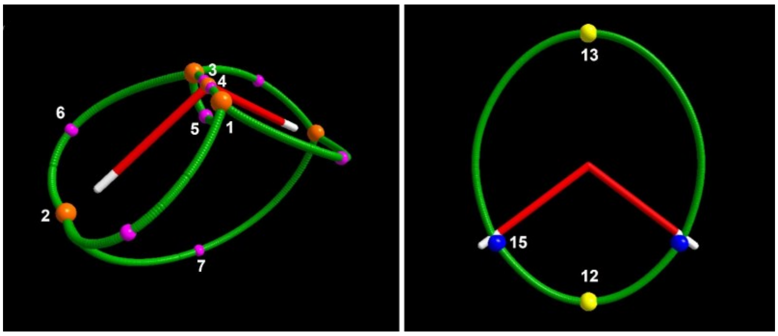

Figure 1: Spin graphs of $^3B_1$ water molecule at CASSCF(8,8) level of theory. Left panel shows spin density maxima joining paths in positive spin density regions while right panel shows spin density minima joining paths in negative spin density regions. In both panels the molecular graph, associated with $\nabla\rho$ bonds paths, is shown for comparison.

[1] Bader, R.F.W. (1990). Atoms in molecules: A quantum theory. In: *International Series of Monographs on Chemistry*, vol 22. Oxford University Press: Oxford, UK.

[2] Popelier, P.L.A. (2016). On Quantum Chemical Topology. In: Chauvin, R., Lepetit, C., Silvi, B., Alikhani, E. (eds) Applications of Topological Methods in Molecular Chemistry. Challenges and Advances in Computational Chemistry and Physics, vol 22. Springer.

[3] Bruno, G., Macetti, G., Lo Presti, L., Gatti, C. (2020). Spin Density Topology. *Molecules*, *25*, 3537.

OR114

Ordered assemblies of bis-perylene derivatives on metal single crystals

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The assembly of molecular building blocks on crystalline surfaces into ordered nano–architectures is an established approach towards the creation of novel materials with outstanding properties. The surface science methodology allows to investigate the morphology of novel molecular structures in the monolayer or sub-monolayer regime (e.g. self-assembled long range ordered 2D networks), and their electronic properties (e.g. density of states, charge transfer, HOMO-LUMO coupling). Eventually it may lead to a clear understanding of the molecule–to–substrate adsorption geometry together with the interaction between the first layer and the hosting surface. Recently reported O-doped polycyclic aromatic hydrocarbons (PAHs) bearing pyranopyranil or furanyl core showed exceptionally high emission yields and tunable optoelectronic properties, resulting as appealing candidates for photoelectronic applications.[1] Molecular derived electronic states of this class of extended molecule can be disclosed and revealed with the ARPES based momentum mapping methodology[2] with the support of complementary techniques such as Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED). That allowed to shed light on most of the unknown of these π-conjugated systems sorting out the adsorbates electronic structure and their geometric arrangement. Molecular patterns of a specific group of bis-Perylen derivatives are self-assembling on Cu(111) forming ordered extended domains and expressing the mutual recognition of molecules with opposite chirality.[3] Similar assemblies on Au(111) have been studied following the doping route with alkali metal. Subsequent Potassium (K) evaporations have filled the empty molecular states.

[1] T. Miletic, A. Fermi, I. Orfanos, A. Avramopoulos, F. De Leo, N. Demitri, G. Bergamini, P. Ceroni, M.G. Papadopoulos, S. Couris, D. Bonifazi, Chemistry A European Journal 23, 2363–2378 (2017)

[2] P. Puschnig, S. Berkebile, A.J. Fleming, G. Koller, K. Emtsev, T. Seyller, J.D. Riley, C. Ambrosch-Draxl, F.P. Netzer, M.G. Ramsey. Science 326, 702–706 (2009)

[3] G. Di Santo, T. Miletić, M. Schwendt, Y. Zhou, B. M. Kariuki, K. D. M. Harris, L. Floreano, A. Goldoni, P. Puschnig, L. Petaccia, D. Bonifazi, *J. Phys. Chem. C* 125, 44, 24477–24486 (2021)

OR115

On the use of simple computational models to interpret SERS spectra of adsorbed molecules: case studies

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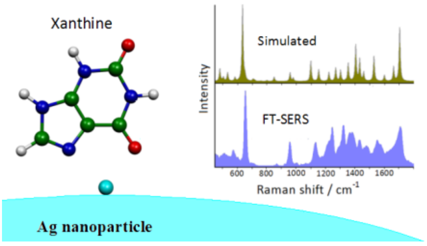
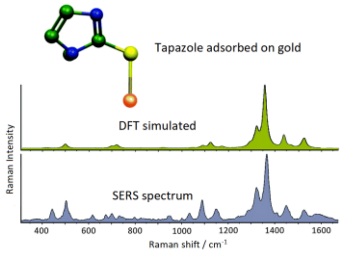
The SERS (surface-enhanced Raman scattering[1]) effect is generally considered due to both electromagnetic and chemical contributions. The former, which usually provides Raman enhancement factors up to 10^7, allows pinpointing the spectra of molecular submonolayers adsorbed on metal surfaces of appropriate roughness. Instead, the latter depends on the change of the molecular polarizability due to the formation of complexes between the active sites of the metal surface and the adsorbing molecules, when the two are separated by distances of about 2 Å. While the electromagnetic contribution plays a predominant role for the SERS enhancement, the chemical contribution is important to determine the SERS spectral *shape*, because the formation of surface complexes by chemisorption causes significant frequency shifts of the SERS bands with respect to the normal Raman spectra, along with changes in the relative intensities.

In this respect, density functional theory calculations allow interpreting the SERS spectra[2] of molecules adsorbed on silver and gold, for instance the anchoring mechanism and geometry. Indeed, the complete simulation of a SERS spectrum is a difficult task due to the need to model a vast surface at the quantum level and computing the vibrational frequencies of such system.

However, it is actually possible to recover the SERS spectrum's *shape* with simple *ad hoc* models, by considering molecules linked to appropriate adatoms of the metal surface. Also, this kind of modeling also allows the recovery of other concomitant effects, such as resonance effects[3] or the possible occurrence of photoreaction products[4,5].

In this presentation, a number of case studies are described, showing both the pros and cons of this approach and the variety of systems that it can interpret.





[1] E.C. Le Ru, P.G. Etchegoin, *Principles of Surface-Enhanced Raman Spectroscopy and Related Plasmonic Effects*, Elsevier, 2009.
[2] M. Muniz-Miranda, F. Muniz-Miranda, A. Pedone, Spectroscopic and computational studies on ligand-capped metal nanoparticles and clusters, in *Metal Nanoparticles and Clusters,* Deepak, F.L. (Ed.), Springer, pp. 55-87, 2017.
[3] F. Muniz-Miranda, A. Pedone, M. C. Menziani, M. Muniz-Miranda, *J Phys Chem A* (submitted).
[4] F. Muniz-Miranda, A. Pedone, M. Muniz-Miranda, *Spectrochimica Acta Part A* 190 (2018) 33-39.
[5] M. Muniz-Miranda, F. Muniz-Miranda, A. Pedone, *Chemistry Select* 3 (2018) 8698-8702.

OR117

Structure drives synchronization in arrays of diffusively coupled self-oscillating droplets

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Networks of diffusively coupled inorganic oscillators, confined in nano- and micro-compartments, represent a powerful tool for studying collective behaviours observed in biological systems.
By taking advantage of microfluidic techniques, we study the dynamics of arrays of diffusively-coupled Belousov-Zhabotinsky (BZ) oscillators encapsulated in water-in-oil single emulsions [1] and in water/oil/water (w/o/w) double emulsions (DEs) [2].
In single emulsions new synchronization patterns are controlled by modulating the structural and chemical properties of the phospholipid-based membranes confining the BZ microoscillators. Changes are induced by introducing specific dopants that do not alter their basic backbone of the phospholipid bilayer but modify the membrane lamellarity or react with the chemical messengers. A transition from 2-period clusters (showing 1:2 resonance) to 1-period antiphase synchronization is observed by decreasing the membrane lamellarity, while an unsynchronized scenario is found when the dopant interferes with chemical communication.
In the presence of multi-compartmentalized shells (Des), after an initial induction period, all the oscillators pulsate in phase with halved period with respect to the starting one.

Experimental scenarios are interpreted within a unique kinetic framework including mass-exchange terms to tune the coupling strength among different oscillators.

The impact of delayed feedback, mimicking natural lag that can arise in the communication due to the confinement properties, are also numerically explored by including a time delay in the coupling terms [3]. A direct transition from anti-phase to in-phase synchronization and back to the initial anti-phase scheme is observed by progressively increasing the time delay. Strong similarities of these phase transition dynamics with the synchronization scenarios characterizing the coordination of oscillatory limb movements are also discussed.

[1] M.A. Budroni et al. J. Phys. Chem. Lett. 11 (2020) 2014
[2] M.A. Budroni et al. Chem. Comm. 56 (2020) 11771
[3] M.A. Budroni et al. PCCP 23 (2021) 17606

OR119

Iron oxides and oxyhydroxides as single phases or embedded in porous ordered inorganic supports for arsenic removal from water

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Among the problems the scientific community must face with, pollution is one of the most urgent, further limiting the resources, in particular in terms of water and soils, available for the growing world population. Arsenic represents a critical pollutant, due to its high toxicity in low concentrations and the worldwide contamination of soils and water,[1,2] although different associated risk assessments can be defined based the As speciation. Among the different remediation approaches, adsorption assures high efficiency, low cost, possibility of designing regenerable and versatile multifunctional sorbents. Iron oxides and oxyhydroxides are known to be active phases towards As, and at the same time offer the advantages of being low-cost, biocompatible, eco-friendly, and (some of them) magnetically recoverable.[3] Moreover, when nanostructured the increase in the surface area leads to the possibility to save the amount of applied material. In this work, nanostructured iron oxides and oxyhydroxides were tested as sorbents for As^{III}/As^{V} species from water, in form of single phases or embedded in porous silica supports. Bare akageneite, ferrihydrite, maghemite, and a Fe_2O_3-SiO_2 composite were studied for their As^{V}/As^{III} removal from water in the pH range 2–8.[4] All the systems were characterized for their structure, morphology, texture, and surface charge to correlate them with their performances. The removal experiments showed akaganeite to be the most promising sorbent in the whole pH range for As^{V} and to be also efficient toward As^{III}. Ferrihydrite exhibited the highest As^{III} removal capacity. Key-properties in the removal process were found to be the sorbents' surface chemistry and their ability to modify the starting pH. In addition to the bare phases, Fe_2O_3 was also grown into porous SiO_2 scaffolds as versatile platforms for the development of multifunctional materials. Both meso-(SBA15, pore size (Ø) = 7–8 nm) and macrostructured (MOSF, Ø = 70-120 nm) silica-based supports were developed and tested.[5] The role of SiO_2 texture was recognized in changing the structure and morphology of Fe_2O_3 leading to different efficiency as As removers: more active 4-6 nm Fe_2O_3 nanoparticles for the SBA15, and a mixture of 18–20 nm-hematite/3–5 nm-maghemite for MOSF were obtained. Finally, among the adopted physical-chemical techniques, ^{57}Fe Mössbauer spectroscopy, and DC magnetometry, allowed us to reveal interesting details on the interaction between the pollutant and the sorbent and about the changes in the active phase upon usage.

[1] T. G. Asere et al. Sci. Total Environ. 676 (2019) 706
[2] World Health Organization, Guidelines for Drinking-water Quality, World Health Organization, 4th edn, 2017.
[3] S. Bolisetty et al. Chem. Soc. Rev. 48 (2019) 463
[4] M. Sanna Angotzi et al. Nanomaterials. 12 (2022) 326
[5] M. Sanna Angotzi et al. Nanoscale Adv. 3 (2021) 6100

OR120

Modulation of Cell Redox Balance in HL-1 Cardiomyocytes by Photostimulated Organic Semiconductor Films

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Activable organic polymers can be employed to modulate cell processes and stimulate cell proliferation [1,2]. Several examples have been reported for poly-3-hexyl-thiophene (P3HT) films with cardiovascular cells: for example, photo-activation of P3HT films have been shown to foster angiogenesis of endothelial colony forming cells [3,4] and consequently tubulogenesis was strongly promoted [4].

Several mechanisms have been considered to explain the effects on cellular physiological processes caused by the P3HT photostimulation in water solutions, such as the photo-activated electrochemical production of reactive oxygen species (ROS). In fact, ROS are known to play a main role in many cellular processes [5]. We investigated photo-stimulated production of ROS in aqueous solutions at the solid-liquid electrolyte-P3HT interface [6]. Spatially-resolved production of hydrogen peroxide was obtained by spatially controlling the illumination of P3HT films, and ROS production was studied by SECM at the micrometric scale. As a proof of principle, we studied the interaction of a model redox protein, Cytochrome C, with photostimulated P3HT films; by employing an SECM/fluorescence microscope apparatus, we showed that we are able to control the Cytochrome C redox state at the photostimulated organic semiconductor/liquid interface [6].

We employed SECM to investigate and image ROS production in cells, both under physiological and pathological conditions [7,8] and to evaluate cellular redox balance [9].

We will present also how cytoplasmatic redox balance of HL-1 cells, a cardiomyocyte cell line, is modulated by photo-induced production of ROS by P3HT films on which they grow. SECM was employed to investigate and quantify the effects of ROS local production on single cardiac muscle cells. We also report on the effect of P3HT nanoparticles internalization in HL-1 cell cytoplasm and on the effect of their photostimulation.

Acknowledgements
We acknowledge European Union (H2020-FETOPEN-2018-2019-2020 LION-HEARTED project – No 828984) for foundings.

[1] E. Zucchetti et al. J. Mater. Chem. B 5 (2017) 565-574
[2] F Lodola et al. Sci. Adv. 5 (2019) eaav4620
[3] F. Lodola et al. Sci Adv. 5 (2019) 1–13
[4] F. Moccia Front Physiol. 11 (2021)
[5] H. Sies et al. Nat Rev Mol Cell Biol 21 (2020) 363–83
[6] I.A. Aziz, M. Malferrari, et al. iScience 23 (2020) 101091
[7] M. Malferrari et al. Anal. Bioanal. Chem. 411 (2019) 4365-4374
[8] M. Malferrari et al. ChemElectroChem 6 (2019) 627–633
[9] S. Rapino et al. Electrochim Acta. 179 (2015) 65–73

OR121

Water reactivity on Schreibersite: a reservoir for prebiotic living phosphorus

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Phosphorus is an element of primary importance for all living creatures, being present in many biological activities in the form of phosphate (PO_4^{3-}). However, there are still open questions about the origin of this specific element and on the transformation which allowed it to be incorporated in biological systems. The most probable source of prebiotic phosphorus is the intense meteoritic bombardment during the Archean era, few million years after the solar system formation, which brought tons of iron-phosphide materials (schreibersite) on the early Earth crust [1]. It was recently demonstrated that by simple wetting/corrosion processes from this material various oxygenated phosphorus compounds are produced [2]. In the present work, the wetting process of schreibersite (Fe_2NiP) was studied by computer simulations using density functional theory, with the PBE functional supplemented with dispersive interactions through a posteriori empirical correction (D*0) [3,4]. Therefore, the two stable (110) and (001) Fe_2NiP surfaces were used simulating different water coverages, from which structures, water binding energies and vibrational spectra have been predicted. The computed (ana-)harmonic infrared spectra have been compared with the experimental ones, thus confirming the validity of the adopted methodology and models (see Figure 1) [5,6]. Moreover, water reactivity was inspected in several possible deprotonation reactions, also increasing the number of water molecules in order to lead to the formation of phosphonic and phosphoric acids and their corresponding deprotonated forms.

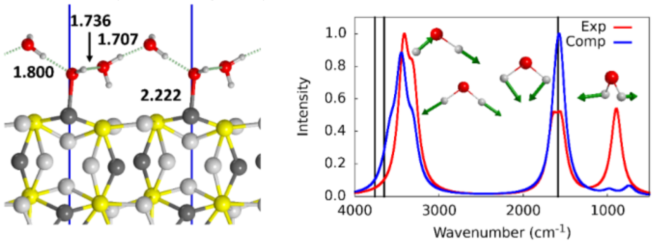

Figure 1: PBE-D*0 optimized geometry of water monolayer on the (110) Fe_2NiP surface (left) and simulated vs experimental IR spectrum (at 125 K). Atom color legend: H in white, O in red, P in yellow, Fe in light grey, Ni in dark grey.

[1] A. Gulick, *Am. Sci.* 43 (1955) 479.
[2] M. A. Pasek and D. S. Lauretta, *Astrobiology* 5 (2005) 515.
[3] S. Pantaleone, M. Corno, A. Rimola, N. Balucani and P. Ugliengo, *ACS Earth Space Chem.* 5 (2021) 1741.
[4] S. Pantaleone, M. Corno, A. Rimola, N. Balucani and P. Ugliengo, *J. Phys. Chem. C* in press.
[5] N. L. La Cruz et al., *Phys. Chem. Chem. Phys.* 18 (2016) 20160.
[6] D. Qasim et al., *J. Phys. Chem. C* 121 (2017) 13645.

OR122

New TDDFT algorithms and strategies for the simulation of optical properties of large metal nanoclusters

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We report about new algorithms and computational protocols for the calculations of optical properties and able to manage large metal clusters, included in the last version of the ADF (AMS) program.

The use of efficient simulation algorithms, the complex polarizability polTDDFT approach [1] and the Hybrid-Diagonal Approximation (HDA) [2], allows us to employ a variety of exchange-correlation (xc) functionals at an affordable computational cost. We are thus able to show, first, how the optical response of this prototypical compound, especially but not exclusively in the absorption threshold (low-energy) region, is sensitive: (1) from a methodological point of view, to the choice of the xc-functionals employed in the Kohn-Sham equations and the TDDFT kernel, and (2) from a chemical-physical point of view, to the choice of the MPC geometry. By comparing simulated spectra with experimental data, we then demonstrate how a hybrid xc-functional employed in both the Kohn-Sham equations and the diagonal TDDFT kernel at the crystallographically-determined experimental geometry is able to provide a consistent agreement between simulated and measured spectra across the entire optical region. Single-particle decomposition analysis tools finally allow us to understand the physical reason of the failure of non-hybrid approaches. Finally we will consider also the Electronic Circular Dichroism (ECD) in plasmonic chiral systems and clusters protected by ligands. The role of conformational dynamics of the ligand will be also addressed.

[1] O. Baseggio, G. Fronzoni, M. Stener, J. Chem. Phys. 143 (2016) 024106.
[2] M. Medves, L. Sementa, D. Toffoli, G. Fronzoni, A. Fortunelli, M. Stener, J. Chem. Phys. 152 (2020) 184102.

OR124

Oxygen redox activity in high-energy P2-type layered oxides cathodes for Na-ion battery: new design principles from ab initio calculations

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Na-ion batteries (NIBs) are rapidly emerging as promising post-Lithium technology for large-scale applications, thanks to the wide availability and low cost of raw materials [1]. Research efforts aiming at developing an effective deployment of NIB technology are mainly focused on the design and optimization of highly efficient active materials, which for the cathode side seem to rely on enhanced energy density and stability [2]. Layered transition metal oxides (Na_xTMO_2) have shown outstanding performances as high-energy cathode materials in NIB cells and exhibited the chance to attain larger specific capacity by enabling anionic reactions at high operating voltage [3, 4]. This represents a new paradigm in the development of positive electrodes, but the $O^{2-}/O_2^{n-}/O_2$ redox processes need to be finely controlled to prevent the release of molecular oxygen and thus huge capacity loss. We report a first-principles investigation of P2-type Mn-defective layered oxides with different metal doping at the TM site (*e.g.*, Ni or Ni and Fe) by means of PBE+U-D3(BJ) calculations. Structural and electronic features are dissected for each redox-active element in $Na_xNi_{0.25}Mn_{0.68}O_2$ (NNMO) and $Na_xFe_{0.125}Ni_{0.125}Mn_{0.68}O_2$ (NFNMO) materials as function of sodiation degree corresponding to different states of charge. We address the oxygen redox activity by considering the formation of oxygen vacancies and dioxygen metal complexes at low Na loads (*i.e.,* high voltage range). Low-energy superoxide moieties with different coordination geometries are predicted to be formed at x Na = 0.25 in Mn-deficient sites, while the x Na = 0.125 content enables the release of molecular O_2 via preferential breaking of Ni-O bonds. Mechanistic insights show that dioxygen formation is driven by the M-O covalency and unveil that O_2 loss can be effectively suppressed by Fe doping. Our findings pave the route for the rational design of high-energy Na_xTMO_2 cathodes that feature enhanced reversible capacity and thus boost the development of efficient NIB devices. These outcomes are subject of recent scientific publication on *ACS Energy Letters* and *Journal of American Ceramic Society* [5, 6].

[1] B. Dunn, et al., Science, 334, 6058 (2011) 928-935
[2] Y. Huang, et al., ACS Energy Lett., 3, 7 (2018) 1604-1612
[3] Q. Wang, et al., Nat. Mater., 20, 3, (2021) 353-361
[4] M. Ben Yahia, et al., Nat. Mater., 18, 5 (2019) 496-502
[5] A. Massaro, et al. ACS Energy Lett., 6 (2021) 2470-2480
[6] A. Massaro, et al. J. Am. Ceram. Soc., 1 (2022)

OR125

Improved efficiency and stability of Perovskite Solar cell/modules with opaque and semitransparent layout

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Scalable fabrication of efficient large area Perovskite solar cells (PSCs) and modules (PSMs) with high stability against light soaking and thermal stresses on both opaque and semitransparent forms are important aspects that still need to be properly addressed through innovative approaches. In our activities, several approaches to reach efficient and highly stable PSMs on opaque and semitransparent forms have been developed. Among the first track records for realization of stable PSMs In 2017, 350 h light stable PSM fabricated out of glove box by using crystal engineering (CE) method and reaching an efficiency 13% and 12.1% using Spiro-OMeTAD and Poly(3-hexylthiophene-2,5-diyl) P3HT as hole transport materials (HTM), respectively.[1] Later, by identifying a specific doping strategy of the P3HT polymer, a 13.3% efficient large area module (43 cm^2 AA) was fabricated with thermal stability of >500 h T80 at 85 °C and >100 h T90 stability against continuous light soaking and (>1500 h) shelf life stability was achieved for the device.[2] Moreover, by considering a scalable CE approach based on solution heteroepitaxial growth of stable mixed cation/anion hybrid perovskite thin film under ambient conditions, an efficiency of 18.4% for small area (0.1 cm^2), and 12.7% and 11.6% for fully blade-coated modules with an active area of 17 and 50 cm^2, respectively, was achieved.[3] In 2019, an efficiency above 20% on small area and 17% on large area module (43cm^2 AA) maintaining above 90% of the initial efficiency after 800 h thermal stress at 85 °C was demonstrated by exploiting polaron arrangement of tuned polymeric hole transport layer[4]. This results was recently improved with the fabrication of a 45.6 cm^2 AA module with an efficiency of 18.45% and 24% small area using co-solvent stertegy.[5] In addition, by using an universal approach for layer-by-layer deposition of 3D/2D perovskite films with zero waste permitted to fabricate large area cells, efficiency of 19.55%, thermal stability at 85 °C of T90=1000 h and 18.8% efficiency of perovskite solar module.[6] In the present work, extending the reported strategy by using novel stable 2D perovskite passivation layers, we report on the fabrication of high efficiency, stable perovskite solar module reaching and efficiency of 20.2 % and more than 1000 h thermal and light stability. In addition, we also fabricated semitransparent PSCs reaching above 19% efficiency by using a combination of engineering of the polymeric HTLs (doping strategy and polaron arrangement), 2D perovskite passivation and interlayer engineering. In particular, by scaling up this approach, high performance semitransparent perovskite solar modules (ST-PSMs) are fabricated achieving beyond 13% photoconversion efficiency (PCE) on 47 cm^2 AA. The ST-PSM retains more than 90% of its initial PCE after 2000 h light soaking. Indeed, highly stable 4-terminal perovskite-Si multijunction devices may be realized with PCE approaching 30% or even beyond it.

[1] Yaghoobi Nia, N., Zendehdel, M., Cinà, L., Matteocci, F. & Di Carlo, A. *J. Mater. Chem. A* **6**, 659–671 (2018).
[2] Yaghoobi Nia, N. *et al. Small* **15**, 1904399 (2019). 3.Yaghoobi Nia, N. *et al. Nano Energy* **69**, 104441 (2020).
[3] Yaghoobi Nia, N. *et al. Nano Energy* **82**, 105685 (2021).
[4] Zhang, H. *et al. Nat. Commun.* **13**, 89 (2022). 6.Zendehdel, M., et al. *Sol. RRL* (2021). doi:10.1002/solr.202100637.

OR126

Cesium Manganese Bromide NCs as Sensitizer for Downconversion

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Using trivalent lanthanide (Ln^{3+}) ion as emission center and a sensitizer as light absorption center is a common strategy for downconversion emission. Lead halide perovskites meet the demands for downconversion as sensitizer, but they suffer from low visible absorption, poor stability, and toxicity. In this work, we show a downconversion near infrared emission based on lead-free cesium manganese bromide nanocrystals enabling efficient transfer of visible absorbed photons to the low energy near infrared emission centers. For that, we synthesized phase-pure $CsMnBr_3$ and Cs_3MnBr_5 nanocrystals doped with Nd^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+}. Steady-state excitation spectra and time-resolved photoluminescence measurements confirm the correlation of the $CsMnBr_3$ broadband visible absorption to the lanthanides emission. This work reveals $CsMnBr_3$ as a lead-free and efficient sensitizer for developing and designing visible to near infrared downconversion.

[1] H. Bahmani Jalali et al. ACS Energy Lett. (2022) *Just Accepted*

Tuning the magnetic properties of spinel ferrite nanoparticles through chemical composition

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Spinel ferrite magnetic nanoparticles (NPs) (MFe_2O_4; M = Fe^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}...) are a class of inorganic materials studied for their flexible magnetic properties: their structure hosts cations in tetrahedral (A) and octahedral (B) sites, and their cationic distribution (*i.e.*, inversion degree) can heavily change the resulting magnetic properties. Experimental factors like thermal history, surface effects or synthesis method have a large influence on the inversion degree and magnetic properties and require control for a precise study[1], [2]. Chemical engineering of the magnetic properties has been carried out by changing M^{2+} composition[3], [4]; in this work, a set of ~ 9 nm roughly spherical zinc-cobalt ferrite NPs ($Zn_xCo_{1-x}Fe_2O_4$, x from 0 to 0.48) was synthetized by thermal decomposition of organometallic precursors [5]. Their morpho-structural properties were studied by means of X-Ray Powder Diffraction and Transmission Electron Microscopy. Field dependent magnetization loops at 5 K displayed an increase of saturation magnetization (M_s) and a decrease of anisotropy, when Zn^{2+} fraction increases. This was furtherly confirmed by ZFC/FC protocols. Nevertheless, the trend in Ms at 5 K is not respected at 300 K, due to Zn^{2+} effect on the magnetic order resistance to thermal agitation. A better understanding on the process was obtained by measuring the magnetization dependence upon temperature. Eventually, magnetic interparticle interactions were studied by remanence plots (DCD, IRM, δm). All the plots show a downward shifting of the negative peak position and intensity with increasing *x*, pointing out a strong effect on demagnetizing interactions. This opens the way for the application of Random anisotropy Model in order to investigate the magnetic anisotropy and interparticle interactions. [6], [7].

[1] D. Peddis *et al.*, *J. Chem. Phys.*, 2006 , *164714*,
[2] S. Gyergyek, *et al.*, *J. Nanoparticle Res.*, 2010 , *12*, 1263–1273,
[3] V. Mameli *et al.*, *Nanoscale*, 2016 , *8*, 10124–10137,
[4] G. Muscas *et al.*, *Nanoscale*, 2015 , *7*, 13576–13585,
[5] S. Sun *et al.*, *J. Am. Chem. Soc.*, 2004 , *126*, 273–279,
[6] G. Muscas *et al.*, *Phys. Chem. Chem. Phys.*, 2018 , *20*, 28634–28643,
[7] G. Muscas, S. Jovanovi, M. Vukomanovi, M. Spreitzer, en D. Peddis, *J. Alloys Compd.*, 2019 , *796*, 203–209

OR129

Comparative study of magnetic properties of iron oxide nanoparticles with different organic ligands embedded in mesoporous silica structure

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The use of magnetic nanoarchitectures in several applications is often limited by the lack of non-interacting particles[1,2]. Here we report a synthetic strategy of a hybrid nanoarchitecture (i.e., magnetic nanoparticles dispersed in magnetic or non-magnetic matrix) that induce the use of magnetic nanoparticles in a wider range of applications in which less agglomerated particles were required, highlighting the key role of the molecular coating. 5 nm cobalt ferrite nanoparticles prepared by polyol method (CFO_TEG) has been covered by exchange ligand process with dihydrocaffeic acid (HCA). Then, magnetic mesoporous silica nanocomposites have been prepared starting from CFO_TEG (CFO_TEG_Sil) and CFO_HCA (CFO_HCA_Sil), carefully investigating the evolution of morpho structural and magnetic properties of the nanoparticles. Both CFO_TEG_Sil and CFO_HCA_Sil nanocomposites show no difference in saturation magnetization at 5K ($M_s \approx 80(8)$ Am^2Kg^{-1}) within the experimental error, while a variation in reduced remanent magnetization (M_r/M_s) was reported, from 0.73 to 0.62 respectively. On the other hand, a clear difference in nanoparticles dispersion has been observed, particularly CFO_HCA_Sil sample that shows a 47% reduction of interparticle interactions and an increase in the interparticle distance by 23%. This value has been obtained investigating interparticle interactions by remanence techniques showing that this approach can be a good approximation for interparticle distance in case of complex systems.

[1] G. Mohammadi Ziarani et al. RSC Adv. 9 (2019) 25094–25106.
[2] R. Eivazzadeh-Keihan et al. TrAC - Trends Anal. Chem. 141 (2021) 116291.

Laser Processing of Zn_4Sb_3 Thermoelectric Powders

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Fast sintering of thermoelectric powders is a powerful strategy largely used to achieve a nanostructured bulk sample. The nanostructure obtained by fast sintering processes like spark plasma sintering or open die pressing starting from nano-powders, showed improved materials performance also in bulk form. However, thermal stability of the microstructure produced, reproducibility of the performance or effects of the nano-structuring on the resistance to oxidation are limiting factor to industrial exploitation.

The increasing interest on additive solution for 3D building of complex structures is opening an opportunity to grow thermoelectric devices via layer-by-layer sintering of a powder bed. Up to date, such a possibility has been mainly investigated by the group of Saniya LeBlanc of Washington University [1] who realised a built element of chalcogenide through selected laser melting (SLM) The technique used was only partially effective due to the geometrical characteristics of the chalcogenide powder which don't match the technological needs for SLM processing. At the same time some European groups are developing a laser processing with the target of a simultaneous synthesis and sintering of thermoelectric pellets starting from pressed precursors powders [2].

In this work we present the preliminary results of a laser processing of $Zn4Sb_3$ powders. An investigation on the development of the thermoelectric powders to be processed is presented. The main target, is related to achieve a powder fitting the laser processing needs in terms of morphology without involving atomization process. For the investigation of laser processing, the experimental setup has been designed to investigate the effects of different combinations of laser parameters (laser exposure time, incident power and beam size) on the obtained microstructure. Sintering dynamics in the thermoelectric powders have been investigated by SEM and EDS analyses. The thermal effects observed have been used to design a continuous line sintering of the produced powders.

Our work aims to understand the laser processing mechanism on thermoelectric Zn_4Sb_3 in different operating conditions for the development of an effective additive approach, a new perspective for thermoelectric micro-device fabrication.

[1] A. El-Desouky, M. Carter, M.A. Andre, P.M. Bardet, S. LeBlanc, Rapid processing and assembly of semiconductor thermoelectric materials for energy conversion devices, Materials Letters 185 (2016) 598-60

[2] Y. Thimont, L. Presmanes, V. Baylac, P. Tailhades, D. Berthebaud, F. Gascoin, Thermoelectric Higher Manganese Silicide: Synthetized, sintered and shaped simultaneously by selective laser sintering/Melting additive manufacturing technique, Materials Letters 214 (2018) 236-239

OR132

Poster Contributions

Alginate hydrogels filled with keratin/halloysite composite for protective coating of hair and wool

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Composites based on halloysite nanotubes (HNTs) and biomacromolecules (alginate and keratin) were explored as coating materials for the reinforcement and photo-protection of hair and wool fibers, which were treated through the dip coating procedure.

According to our previous work [1], keratin/HNTs mixtures in water are efficient for the protective coating of human hair. Here, we have developed alginate hydrogels filled with both keratin and halloysite for the for the reinforcement and protection of hair fibers. In this regard, the crosslinking of alginate by calcium chloride was tested to obtain a gel system that can be perspective for cosmetic applications. Preliminarily, alginate/keratin/HNTs dispersions were analyzed through ζ-potential, turbidity and dynamic light scattering experiments, while the hydrogel formation was investigated by rheological measurements. The reinforcing action of the hydrogels was estimated by Dynamic Mechanical Analysis (DMA) experiments on the treated hair. The variation of the tensile properties after the UV irradiation exposure allowed us to evaluate the hair protection efficiency of the alginate hydrogel filled with keratin/HNTs composite.

In addition, we investigated keratin/HNTs mixtures for the protective coating of wool fibers used for the fabrication of tapestries. We determined the colorimetric parameters, the thermal behavior, and the tensile properties of the wool fibers before and after their UV irradiation to explore the suitability of keratin/HNTs hybrids for the protective coating of ancient tapestries.

In conclusion, this study demonstrates that alginate hydrogels combined with keratin and halloysite clay nanotubes could be perspective for cosmetic and restoration applications.

[1] G. Cavallaro et al. ACS Appl. Mater. Interfaces 12 (2020) 24348

PO001

Dynamic aspects of protein-aptamer interaction revealed by MD simulation analysis: the case of human α-thrombin

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Oligonucleotide aptamers, short DNA or RNA sequences that bind to their target with high affinity and specificity, are extensively used to modulate the function of most proteins. A particular case is that of the anticoagulant aptamers able to recognize the human α-thrombin (thrombin) by binding the two electropositive regions, known as exosites I and II, lying on the opposite poles of its surface [1]. One of the most extensively studied anticoagulant aptamer is TBA, a 15mer oligonucleotide recognizing the exosite I by adopting an antiparallel G-quadruplex structure [2]. Recently, the interest of researchers moved on a new class of oligonucleotides in which the addition of a duplex-forming sequence to a G-quadruplex module results in an improvement of the binding properties [3,4]. Among them, NU172 possesses a high anticoagulant activity and is the only anti-thrombin aptamer currently evaluated in Phase II of clinical trials [5]. Another interesting duplex/quadruplex aptamer is HD22_27mer that recognizes thrombin exosite II with very high affinity but without exerting a potent antithrombotic activity [6].

Although insightful atomic-level snapshots of the recognition between thrombin and aptamers have been recently achieved through crystallographic analyses [7,8], some dynamic aspects of this interaction were not fully characterized. Molecular dynamics studies of thrombin in different association states, ligand-free and binary/ternary complexes, have been performed [8,9]. The analysis has provided a detailed characterization of the modulation of the inter-exosites communication by anti-thrombin aptamers and a clear evidence of the synergic action of the simultaneous binding of aptamers at the two exosites.

[1] R. Troisi et al. Int. J. Mol. Sci. 22 (2021) 10803
[2] I. Russo Krauss et al. Nucleic Acids Res. 40 (2012) 8119
[3] R. Troisi et al. Nucleic Acids Res. 46 (2018) 12177
[4] I. Russo Krauss et al. Acta Crystallogr. D Biol Crystallogr. 69 (2013) 2403
[5] ARCA Biopharma, Inc. (2011) https://clinicaltrials.gov/ct2/show/NCT00808964
[6] D.M. Tasset et al. J. Mol. Biol. 272 (1997) 688
[7] A. Pica et al. Nucleic Acids Res. 45 (2017) 461
[8] R. Troisi et al. Int. J. Biol. Macromol. 181 (2021) 858
[9] R. Troisi et al. J. Biomol. Struct. Dyn. 39 (2021) 2199

PO002

The effect of the anticancer peptide LL-III on the microstructure and thermotropic properties of cancer model membrane: a calorimetric and spectroscopic study

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The LL-III is an anticancer peptide (ACS) known to exhibit a low toxicity towards healthy eukaryotic cells and high activity *in vitro* against some cancer cell line such as human lymphoblastic leukaemia, human promyelocytic leukaemia, human cervix carcinoma and human colon adenocarcinoma [1]. Previous studies show that it is able to penetrate into cancer cell cytoplasm without altering lipid bilayer integrity, suggesting the existence of an intracellular target [2]. However, the details of LL-III action mechanism are still unknown. Here, the interaction between LL-III and model tumor membrane was investigated by means of calorimetric (differential scanning calorimetry) and spectroscopic techniques (fluorescence emission, fluorescence anisotropy, circular dichroism, EPR). Liposomes composed of a mixture of POPC and POPS or DPPC and POPS were used as simplified model of tumor membrane. The experimental results have shown that LL-III is able to recognize the negatively charged lipid bilayer and adopts an alpha helical structure upon binding. A detailed characterization of the binding mechanism by means of suitable fluorescent probes and EPR experiments has revealed that LL-III interacts with the negatively charged PS lipids at the membrane surface without penetrating in the hydrophobic core. Calorimetric data, further confirmed that LL-III specifically interacts with PS, promoting lipid domains formation. Remarkably, the leakage assay experiment revealed that LL-III exerts a permeabilizing effect on the model membrane in a concentration-dependent manner, possibly due to structural defects existing at lipid domain boundaries. Overall, these results strongly indicated that LL-III acts in the frame of a non-membranolytic mechanism and likely translocate into the cytoplasm by means of transient and local destabilization of the lipid bilayer.

[1] V. Čeřovský et al. ChemBioChem 10 (2009) 2089
[2] J. Slaninová et al. Peptides 33 (2011) 18

PO003

Effect of substrate nanoscale curvature and free energy on the crystallization of polymer thin films

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The assembly of polymer thin and ultrathin films is currently at the focus of intense experimental and theoretical research for both technological and fundamental reasons. Functional polymer films are currently employed in a number of devices for various applications ranging from electronics [1] to biomaterials [2]. Furthermore, the ease of preparation of homogenous polymer films with controlled thickness makes them an ideal system for the investigation of soft materials under nanoscale confinements [3].

Among the parameters which mostly affect the polymer film structure, the surface free energy of the substrate is one of the most effective [4-5]. However, most of the investigations focused on the interactions between the polymer and the substrate, are limited to planar substrates although some reports have shown that the substrate nanoscale geometry might also significantly influences the polymer self-assembly [5].

Here we present a systematic investigation on the combined role of substrate free energy and nano-curvature on the deposition and crystallization of poly-3-hexylthiophene (P3HT) thin films. In particular, by combining ex situ characterizations, performed either after the film deposition or after the film equilibration, and in-situ characterizations, performed during the film equilibration, we will show how the substrate nano-curvature influences both the crystal growth [7] and orientation [8]. Our results demonstrate that two main forces, namely the crystallization enthalpy and the surface free energy minimization, drive the polymer self-assembly. Therefore, ultrafine control of the polymer film structure might be attained by thorough tuning of the substrate properties.

[1] D. Li et al. Adv. Mater. 30 (2018) 1704738
[2] R. Balint et al. Acta Biomater. 10 (2014) 2341
[3] M.D. Marvin et al. Soft Matter 10 (2014) 3166
[4] G. Li Destri et al. Macromol. Chem. Phys.212 (2011) 905
[5] G. Li Destri et al. Langmuir 28 (2012) 5257
[6] G. Yager et al. Soft Matter 11 (2015) 5154
[7] R. Ruffino et al. J. Phys Chem C 123 (2019) 8967
[8] R. Ruffino et al. Polymer 230 (2021) 124071

PO004

A versatile approach of advanced surface modification for applications in the environmental protection

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Nowadays the presence of pollutants in water represents an ever greater and difficult problem to solve. Efficient removal of these contaminants from the aqueous solutions requires advanced oxidation processes (AOPs). This can be accomplished by different methods, such as electrocatalysis, photocatalysis and photo-electrocatalysis, involving the use of materials that allow the fast removal of the pollutants with high degradation percentages. The photo-electrocatalytic approach appears to be among the most promising processes, because it combines the advantages of photocatalysis and electrocatalysis [1].

The most used material in this regard is TiO_2, which however shows several problems including a band gap around to 3.0-3.2 eV that does not allow the absorption of visible light.

With appropriate surface modifications such as the presence of anions like PO_4^{3-}, it is possible to improve the generated photocurrent [2] to obtain a best performing material.

For this reason, in this work the surface of nanostructured TiO_2-based films were chemically modified to improve the electro, the photo-electro and the photocatalytic performance. In particular, the mesoporous TiO_2 film was engineered using the zirconium phosphate (ZP) modification [3] to improve the sensitivity to sunlight, the electrical properties, and the thermal stability of the material (Figure 1).

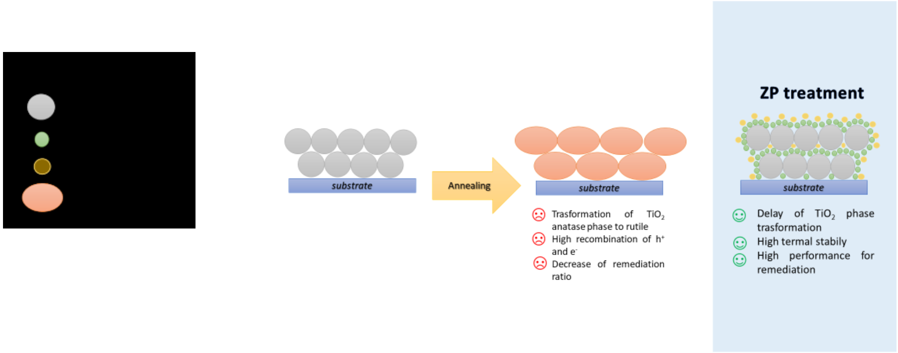

Figure 1 – Schematic representation of TiO_2 engineered surface

The surface functionalization of the samples was verified by using TOF-SIMS, which allows to obtain spatially resolved 3D chemical information. This gives the opportunity to get the information necessary for an efficient engineering of the material in order to obtain the best performances for the required function. Morphology, structure and properties of the samples were studied by means of different techniques, such as SEM, XRD and UV-DRS.

[1] T.H. Jeon et al. ACS Catal. 8 (2018) 11542–11563.
[2] L. Jing et al. Energy Environ. Sci. 5 (2012) 6552–6558.
[3] S. Vitale et al. J. Vac. Sci. Technol. B. 34 (2016) 03H110.

PO005

Lithium halogenides as redox mediators in Li-O_2 batteries: solvent-dependent behavior and parasitic chemistry

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Lithium-oxygen batteries are targeted as promising energy storage systems for large scale applications like vehicles and grids, thanks to their large theoretical energy density (3500 Wh/kg) which is an order of magnitude higher than current lithium ion batteries [1]. Many drawbacks hinder full development of these systems, including high overpotentials and low coulombic efficiencies. Moreover, parasitic reactions, primarily those involving singlet oxygen evolution, are significantly detrimental and imply irreversible damages of cell components. Lithium halogenides LiI and LiBr are promising redox mediators able to reduce charge overpotential and enhance reversibility [2,3]. Nevertheless, the impact of mediators on the electrolyte degradation and in general on parasitic chemistries is largely unknown. We carried out computational calculations that support feasible pathways to singlet oxygen evolution during the oxidation of lithium peroxide mediated by iodine. These theoretical models have been coupled by the experimental study of LiI and LiBr in Li-O_2 batteries, as co-salts in LiTFSI 1M/TEGDME and LiTFSI 1M/DMSO electrolytes. Charge voltage profiles suggest that degradation reactions occur in both solvents with LiI, and their onset potential depends on solvent properties and salt concentration. Analogue degradation profiles are observed when LiBr is used in DMSO, while no evidence of side reactivity has been observed using LiBr in the TEGDME-based electrolyte.

[1] Chem. Rev. 2020, 120, 6626–6683.
[2]J.Mater.Chem.A,2015,3,8855.
[3] Energy Environ. Sci., 2016, 9, 2334-2345.

PO006

Lead-Free and Bio-based $BiFeO_3$/Nylon-11 nanocomposite as potential Piezoelectric Energy Harvesting Device

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Piezoelectric Nanogenerators (PENGs) are an emerging technology for the conversion of mechanical energy into electricity, which could be used to power small devices or microelectronic systems [1]. Nowadays, the most performant piezoelectric energy harvesting devices are based on lead-containing ceramics [2], which however limit their field of application due to lead known toxicity [3]. Among the lead-free piezoelectric materials, bismuth ferrite ($BiFeO_3$) is emerging as an interesting alternative thanks to its versatile crystalline structure and appealing physical properties [4]. Indeed, $BiFeO_3$ is one of the few single-phase multiferroic compounds which simultaneously shows antiferromagnetic, ferroelectric and piezoelectric behaviors at room temperature [5]. One of the main disadvantages regarding the use of $BiFeO_3$ is that the preparation of its pure phase is difficult due to the loss of Bi^{3+} ions during the sintering process. To overcome this problem, $BiFeO_3$ in form of nanoparticles (NPs) can be prepared, thus reducing the sintering temperature required for the synthesis [4]. Furthermore, mixing nanoparticles with polymer matrix can simplify the preparation of thin and flexible films and improve the final outputs of the devices [6]. The polymeric matrices generally used for the preparation of PENGs are polydimethylsiloxane (PDMS) or polyvinylidene fluoride (PVDF) [6, 7]. Nevertheless, in recent years another polymer is gaining attention thanks to its piezoelectric properties: Nylon-11. Nylon-11 (or Polyamide-11, PA11) is a bio-based polymer obtained through the polymerization of 11-aminoundecanoic acid, which in turn is produced from castor beans [8]. It is characterized by a high melting temperature (190 °C) and a relatively large piezoelectric coefficients, which in turn depend on its final crystalline structure [9]. Indeed, Nylon-11's δ'-phase is the most recognized phase as being the one showing highest piezoelectric outputs, thanks to the poor organization of its internal hydrogen bonds [9].

Here we report the fabrication of a nanocomposite based on lead-free $BiFeO_3$ nanoparticles (NPs) dispersed into bio-based Nylon-11 polymer. $BiFeO_3$ NPs homogeneously dispersed into Nylon-11, while the polymer easily crystallized in its δ' piezoelectric phase. These outcomes demonstrate that the incorporation of $BiFeO_3$ NPs nanoparticles in PA11 allow the formation of the piezoelectric δ'-phase resulting in a potential lead-free and bio-based $BiFeO_3$/Nylon-11 PENG devices.

[1] X. Cao et al. Adv. Funct. Mater. 31 (2021) 2102983
[2] X. Niu et al. ACS Sustain. Chem. Eng. 7 (2019) 979
[3] J. Koruzaet al. J. Materiomics 4 (2018) 13
[4] J. Wu et al. Prog. Mater Sci 84 (2016) 335
[5] N. Wang et al. Nano Micro Lett 12 (2020) 81
[6] X. Ren et al. ACS Appl Mater Interfaces 8 (2016) 26190
[7] A. Tuluk et al. J. Alloys Compd 868 (2021) 159186
[8] B. Herzog et al. in Ullmann's Encyclopedia of Industrial Chemistry Wiley (2020) 1
[9] A. Datta et al. Adv. Funct. Mater. 27 (2017) 1604262

PO007

Synthesis of $(Ni_xCo_{1-x})_{33}Fe_{67}$ ternary alloys by topochemical reduction in hydrogen of $(Ni_xCo_{1-x})Fe_2O_4$ nanostructured mixed ferrites

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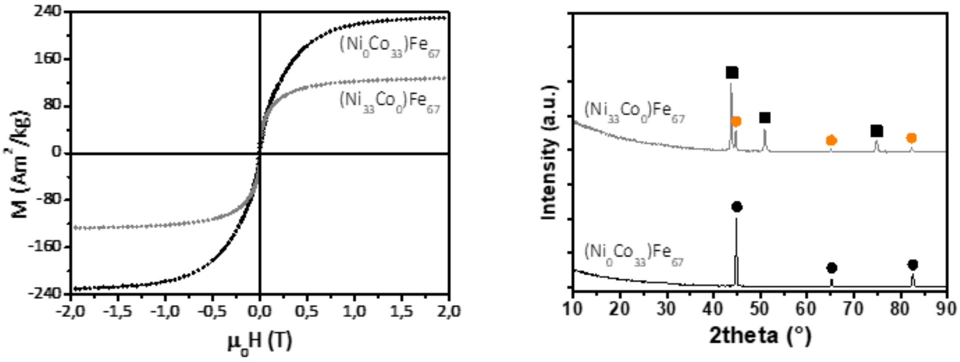
Interesting magnetic properties such as a good magnetic saturation M_s and a good coercivity H_c resulted for the $(Ni_xCo_{1-x})Fe_2O_4$ (x = 0, 0.25, 0.50, 0.75, 1) mixed ferrite, values promising for the energy applications[1]. Since it is well-known that the corresponding $Co_{33}Fe_{67}$ and $Ni_{33}Fe_{67}$ (x = 0 and x = 1) alloys have both a boosted M_s compared to their corresponding oxides, a preliminary investigation of the magnetic properties (Ms, Hc) as a function of these 5 compositions is currently underway. Here, the two alloys have been synthesized at the boundaries of the ternary diagram through an auto combustion sol-gel method followed by a reduction process in hydrogen atmosphere at 500°C for 5 hours. The methods both are simple and scalable to produce powder with nano-sized grains. The phase structures and the saturation magnetizations, respectively measured by X-Ray Powder Diffractometry (XRPD) and Vibrating Sample Magnetometry (VSM), are presented in the figures below. A M_s = 242 Am^2/kg ($Co_{33}Fe_{67}$) and a M_s = 128 Am^2/kg ($Ni_{33}Fe_{67}$) have been calculated by extrapolation for the alloys (the experimental M_s of the samples before reduction are 67 Am^2/kg for the Co-Fe-O and 39 Am^2/kg for the Ni-Fe-O oxides). These results will be implemented further for $(Ni_xCo_{1-x})_{33}Fe_{67}$ at x = 0.25, 0.50 and 0.75 and exploited as a compositional model for designing materials destined to further energy-related applications.



(Left) Hysteresis loop and (right) XRD patterns of $(Ni_xCo_{1-x})_{33}Fe_{67}$ at x = 0 and x = 1; The black circles, black squares and orange circles correspond respectively to the Fe bcc, the Fe-Ni bcc and the Fe-Ni fcc structures.

[1] Omelyanchik et al, *J. Mag. Mag. Mater.*, **476**, 2019, pp. 387-391

Machine learning-assisted FTIR analysis of circulating extracellular vesicles for cancer liquid biopsy

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Extracellular vesicles (EVs) are abundantly released into the systemic circulation, where they harbour molecular constituents that provide biochemical information about their cells of origin [1]. As such, EVs are attracting increasing attention as a source of circulating biomarkers for cancer liquid biopsy. Despite this potential, none of the discovered biomarkers has entered the clinical practice so far, and novel approaches for the label-free characterization of EVs are highly demanded. In this regard, Fourier Transform Infrared Spectroscopy (FTIR) has great potential as it provides a quick and informative biochemical fingerprint of EVs [2]. In this pilot study, we investigated, for the first time in the literature, the ability of FTIR to distinguish between EVs purified from sera of cancer patients and controls based on their mid-IR spectral response. For this purpose, EVs were obtained from the serum of patients diagnosed with Hepatocellular Carcinoma (HCC) and healthy donors. Our data pointed out the presence of statistically significant differences in the integrated intensities of major mid-IR absorption bands, including the carbohydrate and nucleic acids band, the protein amide I and II bands, and the lipid CH stretching band. Additionally, we used PCA-LDA for the automated classification of spectral data according to the shape of specific mid-IR spectral signatures. The diagnostic performances of the proposed spectral biomarkers were evaluated using multivariate logistic regression followed by a ROC analysis, obtaining large Areas Under the Curve (AUC=0.91, 95%CI 0.81-1.0). Very interestingly, our analyses suggest that the discussed spectral biomarkers can outperform the classification ability of two widely used circulating HCC markers (i.e., AFP and PIVKA-II) measured on the same subjects. This research was funded by the Italian Ministry of Health, grant number GR-2016-02363310.

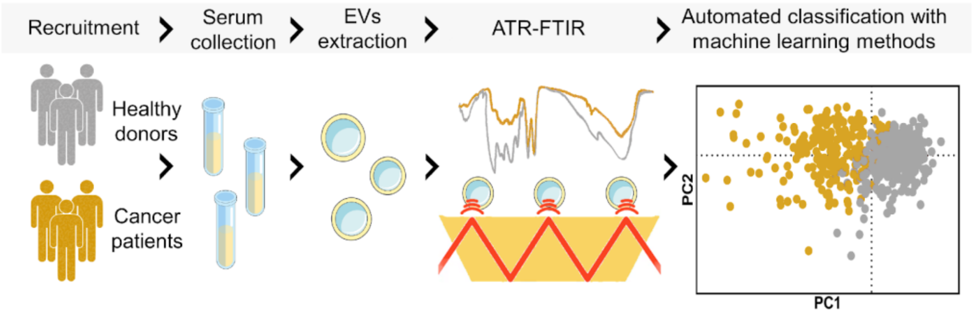

Figure 1. Schematic workflow of the presented EV-based liquid biopsy. Briefly, serum samples from HCC patients and controls were collected. EVs were isolated from serum samples and ATR-FTIR measurements were performed. Finally, automated classification of the two groups was achieved by machine learning analysis of the acquired spectra.

[1] Di Santo R. et al. Nanomaterials 11.6 (2021): 1476.
[2] Romanò S. et al. Analytica Chimica Acta 1140 (2020): 219-227.

PO010

Probing The Ultrafast Dynamics In Biological Systems: The Role Of The Hydrogen Bonds

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It is well known that the establishment of specific and directional interactions could affect the functionality and the dynamics of biological and artificial complex systems. Particular attention has recently been focused on the role that hydrogen bonds (H-bonds) play in changing the dynamical properties of electronic excited states [1,2]. In this work, we investigated the ultrafast relaxation dynamics of a biological pigment-protein complex, the Water-Soluble Chlorophyll-binding Protein (WSCP), to probe and verify how the presence of H-bonds could affect the photophysics of the excited state. 2D-Electronic Spectroscopy was applied for this purpose since it allows to follow the ultrafast dynamics of complex systems, providing information on the temporal evolution of both coherent and non-coherent processes with a time resolution in the order of femtoseconds.

We found that the directional nature of H-bonds has important implications for the electronic properties of the WSCP: the electronic properties of the pigments, namely the transition dipole moment and then also the electronic coupling and the excitonic energy gaps are tuned by the presence of specific and directional interactions between the protein backbone and the formyl group on the Chl *b* moiety [3]. These findings suggest that the design of H-bonded structures implies the possibility of tuning the photophysics and the transport properties of complex systems by engineering specific interactions with the surroundings.

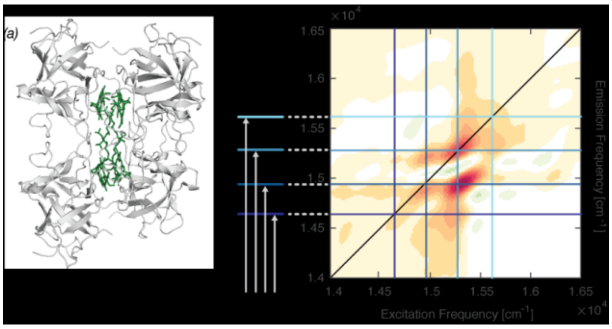

Figure 1. (a) Crystallographic structure of WSCP where the Chl tetramer is recognizable. (b) The 2D-DAS of Chlb-WSCP obtained from the global fitting procedure, where the four excitonic energy levels are highlighted.

[1] Llansola-Portoles, M. J.; Li, F.; Xu, P.; Streckaite, S.; Ilioaia, C.;Yang, C.; Gall, A.; Pascal, A. A.; Croce, R.; Robert, B. Biochim. Biophys. Acta, Bioenerg. 1861, 148078 (2019).
[2] Sturgis, J. N.; Robert, B. J. Phys.Chem. B, 101 (37), 7227−7231 (1997).
[3] E. Fresch, E. Meneghin, A. Agostini, H. Paulsen, D. Carbonera, and E. Collini, J. Phys. Chem. Lett. 11, 1059 (2020).

PO011

X-Ray Fluorescence spectroscopy, Particle-Induced X-ray Emission and Rutherford Backscattering Spectrometry for gold foil thickness determination

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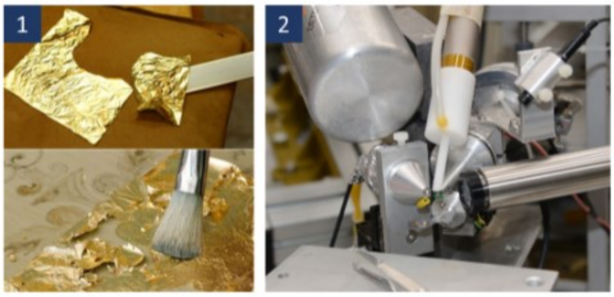
Determining the thickness of metallic coatings can be carried out with several methods; but in the case of art and historical objects, such as gilded surfaces, the method must be non-destructive and the interaction with the sample should imply the minimum amount of energy transfer to the object. X-Ray Fluorescence spectroscopy (XRF) is a very convenient tool for the rapid analysis of metallic components [1,2], can be performed with no or very mild surface cleaning and has the great advantage of being fully portable. In the case of layers having a thickness below that needed to transmit the majority of impinging X-rays (operatively above 95%) the X-ray yield in gold is linear with the thickness and can be calibrated using standards offering a fast and reliable method to determine gold leafs thicknesses up to about 600nm. In this work, Particle-Induced X-Ray Emission (PIXE), Rutherford Backscattering Spectrometry (RBS) analysis and X-Ray Fluorescence have been combined to allow a reliable instrument calibration.

First, preliminary XRF analyses have been performed on gold foils of nominal thickness. Gold foils were produced with gold-beating traditional technology. XRF linearity of the peak-yield/leaf-thickness relation has been verified, within a 10% band. Then RBS with 3MeV protons has measured the real reference foils thickness and its uniformity over the foil surface. Lastly the linearity between the PIXE gold yield and the foil thickness has been verified, demonstrating that the energy loss of the 3 MeV protons in gold is in the keV range and therefore the samples can be considered *thin samples*. We now have a well calibrated XRF system to measure on site gold leafs thicknesses and map their possible superposition for large investigation campaigns on museum collections.



Gold leaf with example of application on wooden object (**Fig. 1**) and PIXE – RBS instrument set-up at Labec (INFN) accelerator (Laboratory of Nuclear Techniques Applied to Cultural Heritage), Radiate Project (**Fig. 2**).

[1] Q. Wu et al. J. Cult. Herit. 49, 211–221 (2021)
[2] C. Fiorini et al. X-Ray Spectrom. 31, 92–99 (2002)

PO012

Functional core- mesoporous shell nanoparticles as photoactive materials

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Core-shell nanostructures consisting of a solid core of functional nanoparticle (NP) and a mesoporous silica shell (MSS) represent versatile generation of nanomaterials able to convey into a single structure multi-functionality useful for applications in different fields including catalysis, adsorption, separation, sensing to biomedicine [1-3]. Superparamagnetic [3], metal [1] NPs with different size, shape or degree of aggregation have been embedded in mesoporous silica structures to combine the magnetic or plasmonic properties of the functional core with the cargo capability of the MSS, characterized by high surface area. Since their first development, different mesophases have been synthesized ranging from hexagonal ordered [4], worm-like disordered, stellate, dendritic and central-radial pores structures [1-3], whose design aims at increasing pore size improving the loading efficiency of large macromolecules and NPs. Here, core structures consisting of plasmonic $Cu_{2-x}S$ NPs with size below 15 nm or spherical non-porous silica NPs embedding luminescent Carbon Dots (C Dots) of about 30 nm have been synthesized and coated with MSS with pore size ranging from 3-4 nm up to tens of nanometers, showing wrinkle-like dendritic and central-radial mesostructures. A soft-template approach has been used to grow the mesoporous structures under basic condition, in the presence of tetraethylorthosilicate (TEOS) using cetyltrimethyl ammonium bromide (CTAB) as surfactant. Monophasic and biphasic soft-template strategies have been explored to modulate the pores structures and the impact of CTAB and TEOS concentration, type of base and organic solvent, has been investigated by a comprehensive morphological, structural and optical characterization. Plasmonic and luminescent mesostructures based on $Cu_{2-x}S$ NPs and C Dots, respectively, have been fabricated and their activity as robust photothermal transducer agents, with additional antimicrobial activity against *Escherichia Coli*, the former, and as optically traceable contrast agent, the latter, demonstrated.

Acknowledgement: This work was developed in the framework of the Bilateral Project CNR-RFBR (Russia) Joint research project (2021-2023) and TITAN-Tumor Immunotherapy by Nanotechnology, Project ID: PON ARS01_00906 | (PVO-704)

[1] X. Du, S. Z. Qiao, Small 2015, 11, 392
[2] C. Xu, C. Lei, Y. Wang, C. Yu, Angewandte Chememie International Edition 2022, 61, e202112752
[3] S. Nemec, S. Kralj ACS Applied Materials Interfaces 2021, 13, 1883
[4] F. Rizzi, R. Castaldo, T. Latronico, P. Lasala, G. Gentile, M. Lavorgna, M. Striccoli, A. Agostiano, R. Comparelli, N. Depalo, M. L. Curri, E. Fanizza, Molecules 2021, 26, 4247

PO013

TiO_2-based nanomaterials assisted photocatalytic treatment for virus inactivation

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The COVID 19 pandemic has highlighted the need of new measures to contain the spread of the virus and bacteria. For instance, the presence of SARS-CoV-2 virus has been reported in fresh-, sea-, and waste-water. Conventional wastewater treatments are inefficient against viruses due to their small sizes and unique surface properties, in addition, some viruses are often quite resistant to common disinfection techniques as UV exposure. In this frame, the use of photocatalytic nanomaterials can be a valuable alternative to chemical disinfectants without the limitation of generating polluting by-products and with the advantage of re-usability in time. In particular, TiO_2 photocatalytic nanomaterial can be a viable water treatment and represent a green sustainable, efficient and low-cost disinfection technique [1]. In this work the ability of TiO_2-based nanomaterials to denature a target model protein, emulating spike protein of SARS-CoV-2, has been investigated.

In details, the TiO_2 P25 photocatalytic denaturation ability has been evaluated by using bovine serum albumin (BSA), as a target model compound. Such a protein has been identified as a model in consideration of the protein nature of the spike structures present on the capsid of SARS-CoV-2, and responsible of infecting target cells. The use of this model system is based on the assumption that the denaturation of the spike protein may prevent infection, thus blocking the spread of the virus. The denaturation of BSA, a high molecular weight protein (M∼66 kDa), has been then monitored to investigate the efficiency of the photocatalytic process assisted by the nanostructured photocatalyst deposited on support.

The experiments have been carried out in aqueous medium and using TiO_2 P25 deposited onto a glass slide under UV light irradiation. Protein denaturation has been monitored by emission spectroscopy (excitation wavelength 270 nm), in the range 290-490 nm, and by electrophoretic technique [2]. Beside the photocatalytic activity, the intrinsic denaturation effect due to the presence of nanomaterial in dark conditions and the effect of UV light have been determined. After 300 minutes a 75% of BSA protein denaturation has been found under UV light assisted by deposited TiO_2 P25, while 30% and 10% of denaturation has been observed under UV and dark condition, respectively.

These results reveal the ability of a TiO_2-based photoactive nanomaterial to denature a protein, thus highlighting its characteristics of a promising antiviral material.

Acknowledgements. This work was partially supported by PON MIUR projects "Energy for TARANTO" (Proposal Code ARS01_00637), ECOTEC (Proposal Code ARS01_00951) and SANITATION (Proposal Code FISR2020IP_01034).

[1] I. De Pasquale et al. Curr. Opin. Chem. Eng. 34 (2021) 100716
[2] K. Malarkani et al. J. Pharm. Anal. 8 (2018) 27-36

PO014

Novel antimicrobial hybrid nanocomposites based on Reduced Graphene Oxide decorated with Ag Nanoparticles

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Hybrid nanocomposites based on graphene and inorganic nanoparticles (NPs) have attracted increasing interest for their technology applications due to the multiple functionalities resulting from the merging of the intrinsic chemical and physical properties of the two components [1]. Graphene is a carbon scaffold with high chemical reactivity, thermal and electrical conductivity, (electro)catalytic activity and high mechanical flexibility [2]. On the other hand, colloidal inorganic NPs are characterized by original size and shape dependent properties and a surface coating layer that endows them for an interesting surface chemical reactivity, which can be further engineered. In this work, novel hybrid nanocomposites based on Ag NPs decorated flakes of Reduced Graphene Oxide (RGO) have been synthesized by a facile *in situ* colloidal approach in aqueous solutions. Initially, RGO has been exfoliated and functionalized with the aminoacidic histidine (His), a biocompatible aromatic linker capable to bind the RGO basal plane via π-π interactions and the Ag NPs by means of coordination bonds. The Ag NPs have been synthesized onto the His-RGO sheets from aqueous solutions by reduction of silver nitrate ($AgNO_3$) with trisodium citrate ($C_6H_5O_7Na_3$) and sodium borohydride ($NaBH_4$). An exfoliating step has been performed on the RGO sheets in His solutions at different pH subsequently the Ag NPs have been synthesized at different pH, RGO:$AgNO_3$ w/w and $AgNO_3$:$C_6H_5O_7Na_3$ and $NaBH_4$:$C_6H_5O_7Na_3$ molar ratio. An investigation of the spectroscopic and morphologic characteristics of the prepared nanocomposites has been performed by means of UV-Vis absorption and Raman spectroscopy, TEM and SEM-EDS in order to identify the most suited conditions for exfoliating RGO sheets and for optimizing the coating density of the sheets with Ag NPs. The obtained His-RGO/Au NPs nanocomposites show a good colloidal stability in water, and reveal an effective exfoliation of the His-RGO sheets in few layers, that result coated by spherical Ag NPs ca. 24 ± 4 nm in size and exhibiting LSPR absorption at 366 nm, thus resulting promising for plasmonic, antimicrobial and electronic applications.

Acknowledgments. The authors acknowledge the projects: TRANSISTOR funded by INAIL(Bando BRIC 2019 ID:33), Italian PON Ricerca e Innovazione (2014-2020) ECOTEC (ARS 01_00951), 'Multi-stacked intercalating hybrid PbS quantum dot film/graphene architectures for enhanced photodetectors' (Prot. MAE0065807, MAE00691402020-06-26) funded by MAECI and the TOOL bilateral CNR-MHESR (Tunisia) project funded by CNR.

[1] S. Ahn et al. Adv. Electron. Mater. 8 (2022) 2100672
[2] C. Ingrosso et al. Carbon 182 (2021) 57

PO015

Luminescent Liposomes Delivering Inhibitor of NLRP3 Inflammasome

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NLR pyrin domain-containing 3 (NLRP3) inflammasome is a multimeric cytosolic protein complex that assembles in response to cellular perturbations. NLRP3-driven inflammation contributes to a variety of inflammatory pathologies and disease, including cancers. Inhibition of the NLRP3 inflammasome represents a promising therapeutic approach for the development of targeted treatments for regulating inflammation. Liposomes (LPs) are versatile delivery nanocarriers able to encapsulate hydrophilic, lipophilic and amphiphilic compounds for applications in different fields, as medicine, cosmetics and food [2]. Their final size and morphology depend on their composition and the preparation method.

Here, multifunctional hybrid nanoformulations based on polyethylene glycol (PEG)-LPs co-loaded with a NLRP3 inflammasome inhibitor, namely MCC950, and luminescent carbon-dots (C-Dots) have been prepared by means of a micro-emulsion approach. C-Dots are characterized by size typically less than 10 nm and tunable optical properties [3], excellent photostability, surface-functionalization and prominent biocompatibility, thus resulting promising scaffolds for biosensing, bioimaging, medical diagnosis and real time tacking of therapeutic agents [4]. The resulting LP-base formulations have been characterized in terms of size, morphology, colloidal stability, optical properties and drug encapsulation efficiency [2]. The preliminary results have demonstrated the formation of anionic LPs with an average hydrodynamic diameter of about 140 nm, high colloidal stability in aqueous medium, satisfactory drug encapsulation efficiency (58-93%), and relevant emitting optical properties in the visible region. The effect of LPs, before and after MCC950 loading, on cell viability has been also evaluated by MTS proliferation assay on two different cell lines, namely Hepa-RG and HLC 19 cells. An in vitro study has been also carried out, to investigate on the LPs ability to alleviate the activation of the NLRP3 inflammasome.

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[1] Weiner, N., Martin, F., Riaz, M., Drug Dev. Ind. Pharm. (1989). 15(10), 1523-1554
[2] Scavo, M.P., Cutrignelli, A., Depalo, N., Fanizza, E., Laquintana, V., Gasparini, G., Giannelli, G., Denora, N., Pharmaceutics. (2020). 12(7), 650
[3] Minervini, G., Panniello, A., Fanizza, E., Agostiano, A., Curri, M.L., Striccoli, M., Materials. (2020). 13(17), 3716.
[4] Latronico T, Rizzi F, Panniello A, Laquintana V, Arduino I, Denora N, Fanizza E, Milella S, Mastroianni CM, Striccoli M, Curri ML, Liuzzi GM, Depalo N. ACS Chem Neurosci. (2021). 12(22), 4286-4301.

PO016

Periodic models of ribonucleic acids: a DFT study

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RNA (RiboNucleic Acid) consists of nucleotides sequences (composed by a ribose moiety and bases, namely uracil, adenine, guanine and cytosine) alternating to phosphate groups and constituting a flexible backbone which can be arranged in a variety of single- or double-stranded geometries, including double-helical structures [1].
In this contribution we will show results coming from DFT (PBE and B3LYP) [2,3] based computational methods applied in the study of single stranded RNAs modeled as linear or helical structures; in particular the study is devoted in building periodic models of such kind of important biopolymers and to explore, through the employment of the CRYSTAL code [4]. RNAs starting structures will refer to bare RNA, but the effect of hydration will be carefully investigated too, referring in particular to the obtainment of the energetical features characterizing the hydration processes and how water molecules can influences the possible conformations (defined by several torsional angles such as α,β,γ,δ etc.)[5] in which RNAs backbone can exist. Also, the obtained models will be adopted to investigate the main vibrational features of RNA and to compute the associated Raman spectra to be compared with data coming from past experimental studies [6].

Figure 1: optimized PBE periodic model of uracil based RNA homo-polymer.

[1] W. Saenger Principles of Nucleic Acid Structure; Springer: Berlin, 1984; Chapter 17.
[2] J. P. Perdew et al. Phys. Rev. Lett. 77 (1996) 3865
[3] A. D. Becke J. Chem. Phys. 98 (1993) 5648
[4] R. Dovesi et al. CRYSTAL17 User's Manual (2018) and References therein
[5] H Kruse et al. J. Chem. Theory Comput. 11 (2015) 4972
[6] J. M. Eyster et al. Biopolymers 13 (1974) 2505

PO017

Spatial and molecular organization of long non-coding RNAs via simulations and experimental benchmarks

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Long non-coding RNAs (lncRNAs) are RNA molecules that are not translated into proteins and with a length that ranges from few hundreds to thousands of nucleotides [1]. Despite their lack of coding potential , in the last decade their crucial role in several biological processes (imprinting, lineage, cell proliferation and gene regulation) has been highlighted. The determination and comprehension of their structure and inner dynamics is essential for understanding their modes of interaction with partners in living cells and, consequently, the way they exert their biological function. However, this constitutes a great challenge in biological physical-chemistry due to their size and plasticity that prevents the application of standard structural methodologies (i.e., NMR spectroscopy and X-rays crystallography), with only, up to date, few successful structural studies of such systems. Moreover, the size of these molecular systems prevents their computational investigation using the state-of-the-art methodologies that allow an atomic-level description of lncRNAs arrangement in space. All these aspects fuel the need of a computational methodology able to reconstruct from first principles, at least partially, the overall shape and the internal arrangement of these molecular systems. This would provide a valuable tool for the interpretation of results obtained by the biological community and at the same time, contribute to elucidate the mechanisms and rules of ribonucleic acids spatial organization

With the aim of finding a simplified but still robust way to efficiently reconstruct *in silico* the overall shape and the folding of lncRNAs, we adopted Replica Exchange Monte Carlo (REMC) methodology, coupled to coarse grained (CG) representation of the nucleotides [2,3]. We have focused on the reconstruction of the spatial arrangement and the internal organization of the 660 nucleotides lncRNA Braveheart (Bvht), the only lncRNA for which public small angle X-rays scattering (SAXS) experimental data are available alongside the single nucleotides reactivity according to internal flexibility and accessibility to the solvent (SHAPE, DMS) [4]. The SAXS spectra have been numerically reconstructed from Monte Carlo sampling with excellent agreement with experimental data, whereas a fairly good agreement has been found between reactivities and the obtained computational geometries.

This study, so far, constitutes the first attempt to perform a molecular simulation of a lncRNA and to benchmark it analytically towards experimental data, highlighting its potentialities as well as its limits. This study constitutes a first step towards the comprehension of lncRNAs spatial rearrangement through the synergy between calculations and experiments and an analytical interpretation of experimental data.

[1] A. Zampetaki, A. Albrecht, and K. Steinhofel, “Long non-coding RNA structure and function: Is there a link?,” Front. Physiol., vol. 9, pp. 1–8, 2018.

[2] J. Kim, T. Keyes, and J. E. Straub, “Replica exchange statistical temperature Monte Carlo,” J. Chem. Phys., vol. 130, no. 12, 2009.

[3] S. Whitelam and P. L. Geissler, “Avoiding unphysical kinetic traps in Monte Carlo simulations of strongly attractive particles,” J. Chem. Phys., vol. 127, no. 15, 2007.

[4] D. N. Kim et al., “Zinc-finger protein CNBP alters the 3-D structure of lncRNA Braveheart in solution,” Nat. Commun., vol. 11, no. 1, pp. 1–13, 2020.

PO018

Study of porous polymers for gas separation by means of Solid-State NMR

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Polymers-based membranes are very promising for gas separation, indeed they are appealing alternative systems to industrial energy-intensive processes. Polymers of intrinsic microporosity (PIMs) are a unique class of amorphous polymers, which, because of their rigid structure, cannot pack efficiently leaving free volume, and in particular generating micropores [1]. Since these systems proved to be very effective for gas separation, the development of materials with higher performances is of current interest [2,3]. Obviously, the design of new materials requires a deeper understanding of their structure and dynamics, but also of the interaction between polymers and gases. Solid-State NMR (SSNMR) is one of the most powerful techniques for the structural and dynamic characterization of solid materials, serving as a guidance for the development of new systems with improved gas separation properties. In this work we present a study of triptycene-based polymers containing fluorinated aromatic rings (Fig.1) by means of SSNMR.

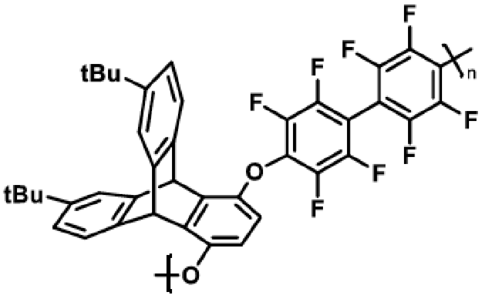

Figure 1 – Chemical structure of the repeating unit of a triptycene-based polymer

The structure was investigated through ^{1}H, ^{19}F Direct Excitation (DE)/Magic Angle Spinning (MAS), ^{13}C{^{19}F} and ^{13}C{^{1}H} Cross-Polarization (CP)/MAS spectra. To get insight into the dynamics of the polymer, ^{1}H and ^{19}F spin-spin (T_2) and spin-lattice (T_1) relaxation times were measured by low-resolution experiments. Moreover, spin-lattice relaxation times of carbon-13 were measured under MAS conditions and high power decoupling from either ^{1}H or ^{19}F nuclei. The analysis of the SSNMR results allowed the main structural and dynamic features of the material to be unravelled.

[1] P. Budd et al. Chem. Commun. 4 (2004) 230
[2] B. Comesaña-Gándara et al. Energy Environ. Sci. 12 (2019) 2733
[3] Y. He et al. Adv. Mater 31 (2019) 1807871

PO019

Plasmonic Metal Nanostructures obtained by Electron Beam Lithography (EBL) for Sensing applications

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Development of optical chemical sensors for detection of specific toxic chemicals at ultratrace levels, analysis of complex mixtures, is crucial for new green and safe technologies. In order to detect minute amounts of a compound in a complex "real-life" sample, sensors must be able not only to differentiate compounds having different molecular sizes but also to identify specific substituents and/or derivative chemical groups attached to the basic structure. [1] Metallic structures reduced to the nanoscale acquire interesting properties such as strongly localizing E fields on their surfaces through the collective oscillations of conducting electrons under stimulation of light at a certain wavelengths. The nanostructures that acquire these characteristics are called plasmonic structures.
Molecules adsorbed onto the surfaces of plasmonic structures experience a strongly enhanced E field due to the localized surface plasmon resonance (LSPR), which amplifies the Raman scattering signal obtained from these adsorbed molecules. This phenomenon is referred to as surface-enhanced Raman scattering (SERS). Because Raman spectra serve as molecular fingerprints, SERS has been intensively studied for its ability to facilely detect trace molecules and provide a chemical analysis of a solution. [2] LSPR manifests themselves in optical resonances, whose frequency is highly dependent on size and shape of the particles, on inter-particles distance, and on surrounding medium. Indeed, the localized plasmon resonances can be tuned to any desired wavelength by varying the particle shape/size and spacing, thus tunning the Raman amplification.[3] As widely investigated in literature, adopting triangular or star shaped metal nanoparticles (NPs) an enhancement of the SERS signal can be obtained with respect to the spherical shaped metal NPs. The electric field becomes in fact intensified at the sharp edges of the metal NPs due to the lightning rod effect. [2] Aim of this work is to study the SERS responses of plasmonic NPs opportunely designed in terms of shape, size and array in order to obtain a versatile sensor that can cover the widest possible range of visible-NIR wavelengths of the Raman scattering signal obtained from adsorbed molecules. To this purpose, EBL was adopted for the fabrication of nanoscaled structures. Thanks to the control of shape, size and distance between contiguous structures at the nanoscale, we are able to tune the LSP resonance of metallic NPs arrays, avoiding surface contamination typical of solution-synthesised NPs especially important for sensing applications. Structural advanced characterization of fabricated NPs are performed by SEM and AFM analysis. Raman measurements are conducted for the SERS analyses.

[1] X. Wang, W. Shi, G. She, and L. Mu, "Surface-Enhanced Raman Scattering (SERS) on transition metal and semiconductor nanostructures," *Physical Chemistry Chemical Physics*, vol. 14, no. 17. pp. 5891–5901, 2012.
[2] T. Y. Jeon, D. J. Kim, S. G. Park, S. H. Kim, and D. H. Kim, "Nanostructured plasmonic substrates for use as SERS sensors," *Nano Convergence*, vol. 3, no. 1. 2016.
[3] E. C. Le Ru *et al.*, "Surface enhanced Raman spectroscopy on nanolithography-prepared substrates," *Curr. Appl. Phys.*, vol. 8, no. 3–4, 2008.

PO020

Resonance energy transfer in micelles: from spectroscopy in solution to multi-photon microscopy in ex-vivo ocular tissues

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The resonance energy transfer (RET) phenomenon has been extensively employed to monitor the fate of nanocarriers in biological systems [1]. Indeed, a RET signal is detected only when the energy donor and acceptor are spatially close, i.e., when the nanocarrier is intact and both dyes are loaded on the same nanoparticle. Upon disaggregation of the nanocarrier, the dyes are expected to move far apart, and the RET signal drastically decreases. Among the different types of nanocarriers, micelles are widely used for several applications, including drug-delivery and bioimaging [2].

In this work, CTAB micelles loaded with DiI and DiD, two indocarbocyanines, have been spectroscopically characterized above and below the critical micellar concentration [3], and then employed in permeation experiments in ex-vivo porcine sclera tissues. DiI and DiD are compatible dyes for RET, since the absorption spectrum of DiD (the energy acceptor) overlaps the emission spectrum of DiI (the energy donor). In aqueous suspension, RET is observed above the critical micellar concentration, and, surprisingly, its efficiency increases below the critical micellar concentration. This counterintuitive phenomenon has been explained with the formation of aggregates containing both dyes [3]. The distribution and the behaviour of the nanocarriers permeated in the scleral tissues have been probed by multi-photon microscopy, monitoring the variations of RET efficiency at different depths in the biological sample. Interestingly, the RET efficiency is significantly amplified at the tissue surface. Guided by the work done on aqueous suspensions, we ascribe the phenomenon to the disruption of micelles as a result of the interaction with the scleral collagen, and the concomitant formation of large dye-aggregates.

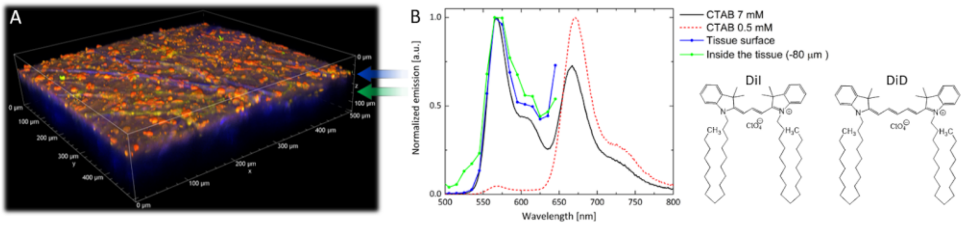

Figure 1 Panel A: 3D rendering overview of a porcine sclera tissue treated with CTAB micelles (7 mM) loaded with DiI and DiD and visualized via multi-photon microscopy (λ_{exc} = 950 nm). Panel B: Comparison between the emission spectra (obtained exciting selectively the energy donor, DiI) acquired from aqueous suspensions of CTAB above and below the CMC and from the treated tissue in correspondence of two different focal planes. The molecular structures of DiI and DiD are also shown.

[1] T. Chen, et al. Adv. Drug Deliv. Rev. 143 (2019) 177-205.
[2] S. Yao, K. Belfield Eur. J. Org. Chem. 17 (2012) 3199-3217
[3] A. Delledonne, et al. J. Mater. Chem. C. 9 (2021) 10952–10964.

PO021

From supramolecular chirality to chiral plasmonic nanoassemblies: towards a unifying theoretical picture

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Chiral nanoassemblies are an emerging research topic, due to their potential applications in chiral sensing and separation, in advanced photonic and spintronic devices or as innovative metamaterials.

Different strategies have been devised to control the chiral assembly at the molecular level [1]. The chiroptical properties (circular dichroism, circularly polarized luminescence, etc) of molecular aggregates are rationalized in the exciton model, that has been recently reconsidered for a critical revision of the exciton chirality rule, commonly adopted to assign the helicity of supramolecular aggregates [1].

Spherical gold nanoparticles can be organized in chiral structures give strong CD signals in the visible due to interaction of the plasmonic modes [2], an intriguing phenomenon that has been addressed theoretically by Govorov [3] in a model that describes the mutual interaction among oscillating dipoles in the nanoparticles. Here we demonstrate that the Govorov's model also applies to supramolecular aggregates, if the tensorial nature of the molecular polarizability is properly accounted for, leading to the same results as the exciton model.

Unifying the models for supramolecular and plasmonic chirality offers a powerful tool to address chirality in mixed molecular-plasmonic structures and to describe technologically relevant phenomena, including the amplification of chiroptical responses in plasmonic-excitonic systems.

[1] N.S.S. Nizar, M. Sujith, K. Swathi, C. Sissa, A. Painelli, K.G. Thomas, *Chem. Soc. Rev.*, 2021, 50, 11208
[2] J. George, S. Kar, E.S. Anupriya, S.M. Somasundaran, A.D. Das, C. Sissa, A. Painelli, K.G. Thomas, *ACS Nano*, 2019, 13, 4392-4401
[3] Z. Fan, A. Govorov, *Nano Lett.* 2010, 10, 2580-2587

PO022

Structure and Dynamics of Crystalline Carbimazole: exploring the powerful combination of Solid State NMR, Quasielastic Neutron Scattering, Molecular Dynamics, and DFT

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In the last two decades, the combination of Solid State NMR (SSNMR), diffractometric techniques and computational methods has been recognized as a powerful tool in the investigation of the structure of crystalline solids, and "NMR Crystallography" is seen as a rapidly maturing subject area in the crystallographic community [1,2]. Furthermore, Solid State NMR is a very powerful tool for the characterization of dynamic properties in solid phases on a broad time scale (form seconds to picoseconds) [3], and in combination with Quasielastic Neutron Scattering (QENS) the range can be extended to shorter times. Even in the case of dynamics, computational methods add a precious tool to achieve a deeper understanding.

In this work, the dynamic and structural properties of the crystalline form of carbimazole (Figure 1), a prodrug used in the treatment of hyperthyroidism, have been investigated in detail. The combination of DFT calculation with ^{1}H and ^{13}C 1D and 2D NMR experiments has allowed the refinement of the drug crystal structure [4], resolving ambiguities in diffraction-derived structures previously reported. The measurement of spin-lattice relaxation times of ^{1}H and ^{13}C nuclei at variable temperatures, QENS and Molecular Dynamic simulations enabled the detailed characterization of the dynamic processes that the carbimazole molecule undergoes in the crystal lattice.

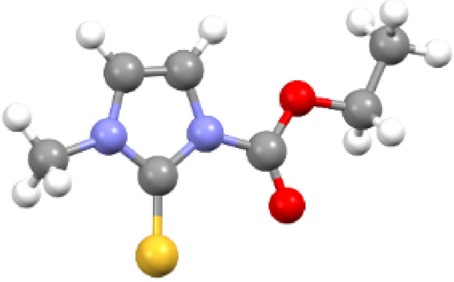

Figure SEQ Figure * ARABIC 1 Molecular structure of Carbimazole

[1] P. Hodgkinson, Progress in Nuclear Magnetic Resonance Spectroscopy 2020, 118-119, 10.
[2] C. Martineau, J. Senker, F. Taulelle, Annual Reports on NMR Spectroscopy 2014, 82, 1.
[3] K. Müller and M. Geppi, "Solid State NMR: Principles, Methods, and Applications" 2021 WILEY-VCH GmbH.
[4] A. Scarperi, G. Barcaro, A. Pajzderska, F. Martini, E. Carignani, M. Geppi *Molecules* 2021, *26*, 4577.

PO023

Perylene Polyphenylmethylsiloxanes: effects of dye content as studied by Solid-State NMR

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Organic dyes represent one of the most desirable systems for the substitution of rare earth ions in light emitting diodes (LEDs). Furthermore, organic dye-based conversion materials are also gaining interest for the development of materials for photovoltaics, such as Luminescent Solar Concentrators (LSCs). Although these materials have a limited stability for optoelectonic applications, their decomposition processes can be minimized if they are embedded in polymeric matrices. In particular, the encapsulation in polysiloxane matrices is particularly attractive both for LEDs and LSCs applications, thanks to several properties of these polymers, including their chemical inertness, thermal stability, high transparency, and tunable refractive index by side group substitution [1,2].
In this work, we have characterized perylene-polyphenylmethylsiloxane systems containing different amounts of a perylene diimide-based dye by means of solid-state NMR spectroscopy. In particular, a perylene diimide dye containing N,N'-diallyl substituents was previously cross-linked to a methylhydrosiloxane-phenylmethylsiloxane copolymer containing terminal and pendant Si-H group by Pt-catalysed hydrosilylation; then, the prepared perylene-polymer system was covalently integrated into a two-component polysiloxane resin containing Si-vinyl and Si-H groups, also in this case by Pt-catalysed hydrosilylation [3]. One-dimensional ^{1}H, ^{29}Si and ^{13}C Direct Excitation Magic Angle Spinning (DE-MAS) and Cross-Polarization (CP)-MAS high-resolution NMR spectra and two-dimensional ^{1}H-^{29}Si HETeronuclear CORrelation (HETCOR) experiments were acquired in order to obtain structural information and to monitor the degree of cross-linking of each sample. Furthermore, low-resolution NMR experiments were applied to measure ^{1}H transverse relaxation times (T_2), which allowed us to gain detailed information about the molecular mobility of each system. A synergic analysis of high- and low-resolution experiments revealed a clear trend of the molecular mobility of the system in dependence of the cross-linking degree.

[1] N. Steinbrück et al. RSC Adv. 8 (2018) 18128
[2] Y. Li et al. J. Polym. Sci., Part A: Polym. Chem. 57 (2019) 201
[3] N. Steinbrück et al J. Polym. Sci., Part B: Polym. Chem. 57 (2019) 1062

PO024

Application of NMR spectroscopy to the study of PFAs removal from industrial wastewaters

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Although water is one of the essential components for life, there is a continuous deterioration of water quality due to numerous anthropogenic activities that result in the introduction of organic, inorganic, and biological pollutants into the various water sources. Of particular concern is fluorinated alkyl substances (PFAs), a class of amphiphilic organic molecules that differ in alkyl carbon chain length and polar functional group at the head of the chain[1]. Since their carbon chain is fully fluorinated, they are very stable and persistent, and they also exhibit hydrophobic and lipophobic properties. The presence of some PFAs in aquatic environment is of greater concern as toxicological data suggests an association to adverse human health effects[2]. For this reason, remediation of PFAs from the environment has rapidly increased; as a matter-of-fact PFAs are recalcitrant to conventional water treatment, adsorption is considered as a better technique due to its cost efficiency, eco-friendliness, and high efficiency[3]. For this purpose, different porous materials, such as silicas, zeolites, clays, resins and active carbon are used. A promising novel material for adsorption of these pollutants is Swellable Organically Modified Silica (SOMS), an organic-inorganic hybrid material[4]. The unique feature of this material is that its structure allows for an expansion of three to five times its volume in the presence of organic compounds, thus enabling their efficient adsorption[5]. During the synthesis, it is possible to functionalize these materials with quaternary amine groups, in order to obtain a positively charged material called QASOMS[6]. In this work, QASOMS was synthesized and used as adsorbent for the removal of three PFAs molecules from water within a concentration range between 50 and 800 ppm. The adsorption property of the hybrid QASOMS material is compared with the performances of commercially available ultra-stable high-silica Y zeolite and granular activated carbon. Perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and perfluorobutanesulfonic acid (PFBS) were used as model PFAs molecules. ^{19}F-NMR analysis was used for the identification and quantification of PFAs. The area of the CF_3 signal of PFOA was used to prepare a calibration curve that was then used for evaluating the PFAS concentration after 24h contact with the sorbent materials. QASOMS showed the highest affinity for all three PFAs compounds, adsorbing them in a greater amount compared to active carbon and Zeolite Y (**Figure 1**).

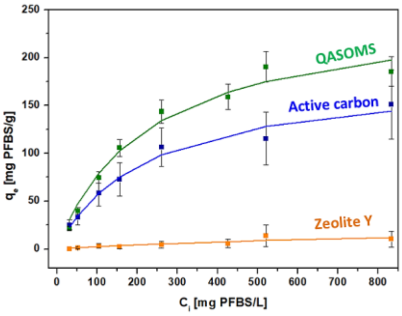

Figure 1 – Adsorption isotherms of PFBS on QASOMS, Zeolite Y and Active carbon.

[1] E. Panieri et al., *Toxics*, vol. 10, n. 2, pag. 44, gen. 2022
[2] I. Ross *et al.*, *Remediation*, vol. 28, n. 2, pagg. 101–126, mar. 2018
[3] D. M. Wanninayake, *Journal of Environmental Management*, vol. 283, pag. 111977, apr. 2021
[4] C. M. Burkett e P. L. Edmiston, *Journal of Non-Crystalline Solids*, vol. 351, n. 40–42, pagg. 3174–3178, ott. 2005
[5] C. M. Burkett, et al., *Chem. Mater.*, vol. 20, n. 4, pagg. 1312–1321, feb. 2008
[6] P. L. Edmiston et al., *Adsorption*, vol. 24, n. 1, pagg. 53–63, gen. 2018

PO025

Interfacial behavior of a new neuroprotective bolaamphiphile: trodusquemine

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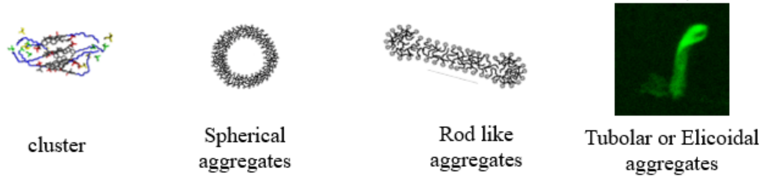
Trodusquemine (Tro) is an aminosterol that modifies the aggregation of the amyloid-β peptides and α-synuclein involved in neurodegenerative disorders such as Alzheimer's or Parkinson's disease [1] and it is presently studied as a neuroprotector drug. In the present work, we studied the aggregation and interfacial behaviour of trodusquemine in solution at physiological pH.

Surface tension measurements and Langmuir monolayer experiments combined with Brewster Angle Microscopy indicates that trodusquemine aggregates in solution as a bolaamphiphile and it forms a stable monolayer at the liquid/air interface. The Tro monolayer shows a reversible transition to a bi- and tri-layer aggregates as function of surface pressure.

Furthermore, ζ potential and DLS measurements unveiled the formation of clusters and aggregates in solution at critical concentrations: three populations, differing in dimensions and surface charge, were found in distinct concentration regimes. Moreover, the aggregation of Tro was evaluated by means of Pyrene and ThT fluorescence experiments monitoring the packing of the aggregates, the dielectric constant and the viscosity of the probe microenvironment. Molecular dynamic simulations of the first steps of aggregation supported the experimental data showing tendency of trodusquemine molecules to aggregate. Confocal and fluorescence anisotropy measurements enlightened the formation of the larger aggregate with different shapes at higher concentration than the critical aggregation concentration.

The body of the measurements provides a comprehensive scheme of the aggregation pathway of the trodusquemine: from the formation of small clusters to the growth of larger spherical and rod-like aggregates. Interestingly, studies on amyloid aggregation as a function of Tro concentration correlates nicely with the aggregation behavior suggesting a possible mechanism of action of the drug.



Schematic representation of the aggregation pathway of the Tro. Inset: chemical structure of Tro at pH 7

[1] R. Limboker et al. Nat. Commun. 10 (2019) 225

PO026

Evidence of reversible oxidation at $CuInSe_2$ grain boundaries

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Chemical instabilities of chalcopyrite surfaces have recently revealed to generate anion vacancies even at room temperature [1]. The arising metastable point defect population explains a common root cause of performance losses in photovoltaic solar cell devices fabricated from this material.

Alkali metal doping and grain boundaries have been at the centre of the attention within the chalcopyrite $Cu(In,Ga)(S,Se)_2$ photovoltaics community for years [2-7].

This study provides the first experimental evidence that the grain boundaries of sodium-doped $CuInSe_2$ thin films may undertake reversible oxidation, whereas undoped films may not. The findings are corroborated by cathodoluminescence imaging [8], secondary ion mass spectrometry and Kelvin probe force microscopy [9] on air-exposed films subsequently subject to vacuum. The solid-gas equilibria open new research questions with respect to the beneficial role played by alkali metal dopants in chalcopyrite solar cells.

This research was funded by the Fonds National de la Recherche Luxembourg through the GALDOCHS project (C14/MS/8302176), by the EU through the nanoTrain for Growth project (713640), and by the University of Genova through the EDICT Curiosity-driven project.

[1] D. Colombara et al., Nature Communications, 11 (2018) 3634
[2] L. Kronik, D. Cahen, and H. W. Schock, Advanced Materials, 10 (1998) 31
[3] Z.-K. Yuan et al., Advanced Energy Materials, 6 (2016) 1601191
[4] A. Chirilă et al., Nature Materials, 12 (2013) 1107
[5] P. Jackson, R. Wuerz, D. Hariskos, E. Lotter, W. Witte, and M. Powalla, Phys. Status Solidi RRL, 10 (2016) 583
[6] D. Colombara et al., Nature Communications, 9 (2018) 826
[7] D. Colombara et al., Journal of Materials Chemistry A, 8 (2020) 6471.
[8] H. Guthrey, et al., IEEE Journal of Photovoltaics, 8 (2018) 1883
[9] N. Nicoara et al., Nature Communications, 10 (2019) 3980

PO027

Understanding the electrochemical features of $ZnFe_2O_4$, anode for LIBs, by deepening its physico-chemical properties

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The search for new anode materials for lithium-ion batteries (LIBs) was stimulated in the last years by the need to find alternatives to graphite, the most employed in commercial LIBs. Anode materials for LIBs are conventionally divided into three groups, on the base of the reaction mechanism with lithium ions: intercalation/de-intercalation, alloying/de-alloying and conversion. $ZnFe_2O_4$ (ZFO) is a cubic spinel, with peculiar functional properties for various applications [1, 2] and was proposed for the first time in 2004 as anode for LIBs [3, 4]. ZFO, unlike other oxides, has a lithium insertion mechanism that involves both conversion and alloying reactions. After the conversion reaction of ZFO with lithium ions and the formation of metallic Zn, Fe, and Li_2O, the obtained Zn can further react with lithium to form a LixZn alloy, thus contributing additional capacity. ZFO is very intriguing thanks to its low cost, abundance and environmental friendliness of both Zn and Fe elements, high surface-to-volume ratio, relatively short path for Li-ion diffusion, low working voltage of about 1.5 V for lithium extraction and, most importantly, high theoretical specific capacity (1072 mA h g^{-1}). Unfortunately, ZFO experiences first-cycle irreversibility and fast decay in the capacity after cycling, mainly due to poor electrical conductivity and large volumetric changes. These issues can be solved thanks to the downsizing of the particles, the addition of proper carbon sources, and to peculiar morphologies. However, the understanding of ZFO electrochemical behaviour is strictly related to a deep knowledge of its physico-chemical properties. In this work, ZFO was prepared by co-precipitation (CP) and template (OX) syntheses, obtaining samples with different morphologies and crystallite sizes. The sample purity was demonstrated by combining X-ray powder diffraction with more sensitive spectroscopic techniques such as Micro-Raman, EPR and Mössbauer. In both the samples, a high purity level was demonstrated, with only traces of hematite in the template sample. The electrochemical features were interpreted on the basis of the determined physico-chemical features, by using conventional electrochemical measurements, but also *operando* X-ray diffraction experiments. It seems that the higher electrode area offered by ZFO-OX with smaller particles is responsible for the better electrochemical reactivity in the first cycles even if, in the long term, a lower crystallinity of the active material, leading to nano-crystalline reaction products, could produce to a better reversibility.

[1] N.A.Masmali et al. Ceram. Int. 47 (2021) 2949
[2] G. Gazzola et al. Mat. Chem.Phys. 273 (2021) 125069
[3] Y.N. Li et al. J. Electrochem. Soc. 151 (2004) A1077
[4] M. Bini et al. Appl. Sci. 11 (2021) 11713

PO028

Functional nanoparticles for Boron Neutron Capture Therapy

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Boron neutron capture therapy (BNCT) is a targeted therapy based on the property of the isotope ^{10}B to capture thermal neutrons with high probability, decaying into a He and a Li nucleus by the capture reaction $^{10}B(n,\alpha)^{7}Li$ and releasing γ ray. If this reaction occurs in tissues, decay products effectively destroy cells due to their high linear energy transfer (LET) properties. Due to their short range of action (about 5–9 µm), cell damage remains almost entirely confined to the cells containing ^{10}B atoms. Neighboring cells containing little or no boron will not be damaged. Therefore, if ^{10}B can be selectively enriched in tumor cells by suitable transport strategies, targeted destruction of malignant cells while sparing healthy tissue is possible.

For the therapy to be effective, ^{10}B must then be conveyed specifically and at an adequate concentration: an interesting and promising approach is to couple boron compounds to nanocarriers, within which boron can be accumulated at high concentrations. Considering the foregoing, the goal of this work was the preparation of functionalized nanomaterials for the neutron capture of boron, in particular hybrid systems resulting from the coupling of boron nitride nanocrystals with mesoporous silica nanoparticles (MNS).

For the synthesis of boron nitride nanocrystals (BNNC), boric acid was chosen as a source of boron and different organic molecules as a source of nitrogen: aliphatic amines, ammonia and melamine. Three different approaches were chosen for the preparation of the hybrid materials: i) the impregnation of MSN with a suspension of previously prepared BNNC; The one-pot synthesis of boron nitride nanocrystals during the synthesis of MSN, followed by ii) classic workup of MSN (filtration, washing and calcination) or iii) hydrothermal treatment in autoclave and following calcination. The characterization of BNNC suspensions, of the siliceous support and of the hybrid materials was carried out using a multi-technique approach that allowed to evaluate dimensions and dispersion properties by dynamic light scattering (DLS) and monitoring the structure by X-ray diffraction and transmission electron microscopy. All the samples, both the suspensions of BNNC and the hybrid materials, were also characterized by electron absorption and emission spectroscopies, to evaluate absorption and fluorescence performance. The integration of the results obtained with the various techniques has allowed us to establish that the applied synthesis methods have led to the preparation of hybrid materials with interesting luminescence properties and great potential for development of multifunctional systems.

PO029

Quick microwave-assisted synthesis of green luminescent carbon quantum dots (CQDs) for light emitting diodes coating

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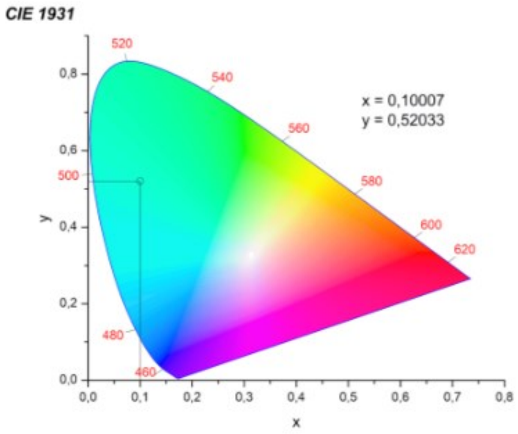
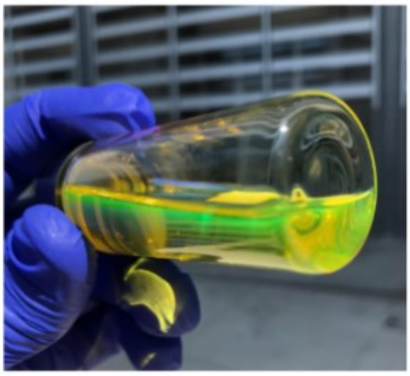
Carbon quantum dots (CQDs) are fascinating luminescent materials that boosted research studies in the past 10 years due to their intriguing properties.[1] Low toxicity and cost coupled with valuable optical properties make CQDs a suitable candidate for the design of many different applications, ranging from solar technologies and optical sensors to photocatalysis and biological implementation. However, the main synthetic approaches of these materials rely on long solvothermal reactions, from 8 up to 24 hours long. Moreover, solvothermal reactions often lead to un-reactant and by-products due to the non-homogeneous heating.[2] Here we present a fast and convenient way to obtain high luminescent green emitting CQDs through microwave-assisted reactions. Terephthalic acid and o-phenylenediamine have been chosen as precursors. The acid-base reactions have been exploited to obtain surface functional groups such as ammine, amides, and carboxylic acids, major responsible of the luminescent properties of the quantum dots. The possible formation mechanism of these carbon-based nanoparticles has been studied by varying the reaction conditions. The obtained CQDs have been well characterized through optical and morphological investigation. Considering the suitable chemical properties of the fluorescent CQDs, a blend of poly(methyl methacrylate) and the nanoparticles has been prepared, allowing the preparation of a green LED (light emitting diode) through a dip-coating procedure.





[1] A. Patra et al. J. Photochem. Photobiol. 37 (2018) 1-22.
[2] H. Lin Angew. Chem. Int. Ed. 57 (2019) 6216–6220.

PO030

Nanotherapeutics for cardiac pathologies: from NP development to their biological behaviour comprehension

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Because of the emerging role of epigenetic dysregulation in heart failure, epigenetic drugs have recently been proposed as a promising approach for the cure of cardiovascular diseases [1]. The development of systems able to encapsulate these drugs and specifically deliver them to the site of interest is essential to reduce drugs toxicity and increase their therapeutic efficacy.

At the same time, characterizing nanoparticles (NPs) protein corona (PC) in dependence of the nano-system physicochemical properties and dynamic blood stream environment is essential to understand NP *in vitro* and *in vivo* behavior [2,3].

Here we aim at developing fluorinated theranostic NPs for the delivery of new epigenetic drugs in the treatment of cardiac pathologies, by exploiting the role of fluorine in 19F-MRI application and in the increase of drug encapsulation efficiency [4]. We produced drug loaded fluorinated PCL-PEG NPs, showing promising therapeutic effects *in vitro* on HL-1 cell line (murine cardiomyocytes). Moreover, we developed a method to study NPs behaviour and biological identity, in physiological blood flow conditions, using a microfluidic system. This method allows efficient isolation and characterization of the NP PC, unravelling the role shear stress and confinement display in the NP-protein interaction.

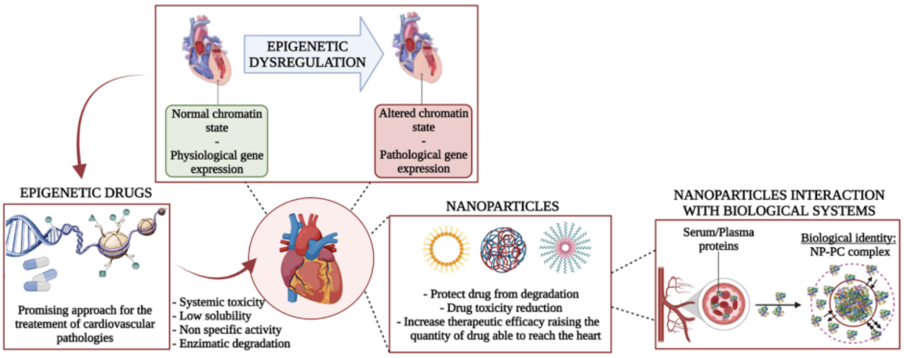

Figure 1. Schematic representation of the role of epigenetic in cardiovascular disease, nanoparticles for drug delivery and the complex series of interactions between environmental proteins and NPs.

[1] C.Pagiatakis et al., Aging Clin Exp Res. (2021) 33(4), 737-745
[2] D. Di Silvio et al., Nanoscale (2015), 28, 11980-11990
[3] M.N. Vu et al., Small (2020), 16, 2002861
[4] G. Neri et al., Chem. Eur. J. (2020), 10057-10063

PO031

Cu_2MnSnS_4 thin films by sputtering technique for photovoltaic applications

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Many efforts have been made word-wide to obtain earth-abundant variants of $Cu_2(In,Ga)(S,Se)_4$ for photovoltaic application. With the most famous Cu_2ZnSnS_4, Cu_2MnSnS_4 (CMTS) has been lately investigated thanks to the manganese's Earth abundancy higher than zinc. [1-3] Here, we present CMTS produced by sputtering the metal's precursors and subsequent sulphurization of the layer in argon atmosphere. A thin layer of cadmium sulphide was deposited by chemical bath deposition to obtain a p-n junction. The device was then finalized with a capping layer of intrinsic zinc oxide, a window layer of aluminum-doped zinc oxide, and an aluminum grid to collect charge effectively. Designed heat treatment on the entire device has been employed in the air atmosphere to enhance the photovoltaic performances. X-ray diffraction and μ-Raman spectroscopy have shown CMTS as the primary phase. Scanning electron microscopy images showed compact and uniform material with a thickness of about 900 nm, and through the energy dispersive X-ray analysis, we confirmed the composition of the final material. J-V measurements on the optimized devices recorded a maximum efficiency of 0.9%. The photoluminescence and external quantum efficiency data analysis identified the detrimental defects acting in working conditions, suggesting paths to improve the photovoltaic properties.

[1] Le Donne et al. Frontiers in Chemistry 7 (2019) 297.
[2] Marchionna et al. Journal of Alloys and Compounds 693 (2017) 95.
[3] Le Donne et al. Solar Energy 149 (2017) 125.

PO032

Cyan Emission in Two-Dimensional Colloidal Cs_2CdCl_4:Sb^{3+} Ruddlesden–Popper Phase Nanoplatelets

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Metal halide (MH) perovskites are one of the most investigated semiconductor materials, with the 3D $CsPbX_3$ structure being renowned for its enhanced optoelectronic performance [1]. Multiple studies are currently attempting to substitute Pb with other elements while still retaining the original properties of this material. This effort has led to the fabrication of MHs of lower dimensionality. Recently, the layered perovskite structures have captured attention for their potential as an emerging class of colloidal semiconductors.

Here we report the colloidal synthesis of the pure Ruddlesden – Popper (RP) phase Cs_2CdCl_4:Sb^{3+}, using a facile hot injection approach. Through strict adjustment of the synthesis parameters, we obtained nanoplatelets with a well-defined size and morphology. The particles underwent extensive structural characterization through synchrotron X-ray diffraction, pair distribution function analysis and transmission electron microscopy. Spectroscopic characterization revealed an intense cyan emission, centered at 510 nm, and with a measured absolute PLQY of 20 ± 5% [2]. The emission is ascribed to the doped Sb^{3+} within the structure and is attributed to an *s-p* transition that originates from self-trapped excitons. This work proves as a confirmation that colloidal synthetic approaches can give access to a new generation of RP phase nanocrystals through halides tuning, metal alloying, the replacement of Cs^+ by alternative counterions and the introduction of various dopants, such as Bi^{3+} or Mn^{2+}.

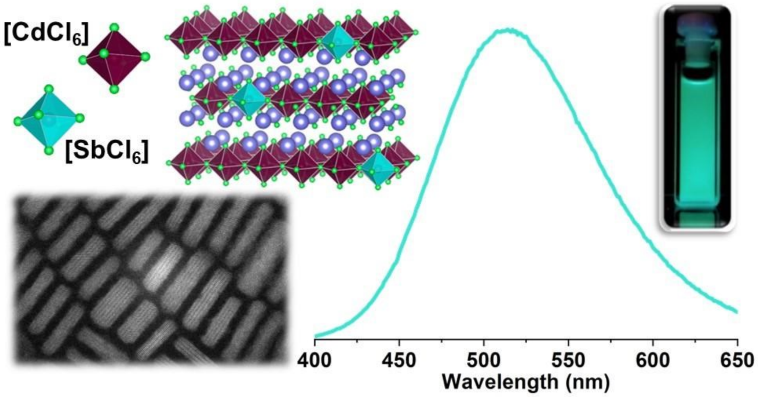

Figure. Crystals structure, TEM image, photoluminescence spectra and under UV lamp of Cs_2CdCl_4:Sb^{3+} nanoplatelets

[1] A. Dey et al. ACS Nano 15 (2021) 10775
[2] F. Locardi et al. ACS Nano 15 (2021) 17729

Magnetic nanoparticles by Laser Ablation and their characterization using a magnetophoretic model

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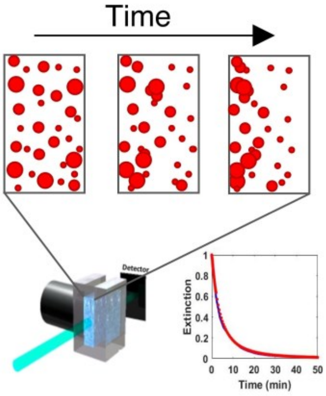
Measurement of the properties of magnetic nanoparticles is mandatory for their application and usually this is accomplished using magnetometers, like SQUIDs or VSMs. However, these techniques require amounts of materials that are not always available and do not allow exploration of new syntheses with low production. The tiny quantity of nanoparticles obtained by laser ablation of strontium ferrite necessitated the characterization of their magnetic properties using an alternative technique, optically detected magnetophoresis, which exploits the motion of nanoparticles in a fluid under a magnetic field gradient. Time dependent optical extinction of a colloidal solution of magnetic nanoparticles can be used for recording the collective motion of the nanoparticles in a fluid. The optical extinction of nanoparticles, with absorption and scattering contributions, depends on the particle material and on their morphologies. We report a new implementation of a magnetophoretic model with the extinction properties of nanoparticles calculated using the Boundary Element Method. The model is applied to estimate the magnetic properties of a challenging sample of mixed ferrite nanoparticles. The results show that, especially for polydisperse samples, the explicit consideration of the size dependent extinction properties of the nanoparticles is needed to characterize magnetic nanoparticles by optically detected magnetophoresis. The motion of magnetic nanoparticles in a fluid, exploited in many applications, is provided with an appropriate description using the present approach.



[1] V. Piotto et al. J. Mater. Chem. C 10 (2022) 3819

PO034

Electroactive polymer films for Bioelectronics: P3HT-MWCNT properties

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One of the main challenges in Bioelectronics concerns the development of materials able to respond to external stimuli and that are compatible with neuronal tissues. In the last decades, conductive polymers (CPs), that were already used in fuel cells and computer displays, have been widely studied and developed as electroactive materials for applications in the biological field. Their conductive properties allow cells or tissues grown upon them to be stimulated, and their “soft” nature lets them form a better biotic-abiotic interface thanks to the elasticity of polymeric films that is similar to the typical one of biological tissues. CPs’ physical and electrical properties can be optimized through the formation of composites enriched with carbon nanotubes (CNT) or graphene in order to improve electron transport capacity, decrease impedance and increase flexibility. Also, their biocompatibility can be improved using methods of functionalization with biologically active molecules.

In this work, we report methods to obtain electroactive nanocomposites using semiconducting regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT), with small percentages in weight of multi- and single-walled carbon nanotubes (MW-CNT, SW-CNT) and reduced graphene-oxide (rGO). As the P3HT-MWCNT-based film systems appear to be the most promising ones for the conductivity properties, the attention has been focused on them. In particular, their morphology and mechanical properties (Young’s Modulus) have been investigated by means of Atomic Force Microscopy (AFM), while their interaction different extracellular matrix proteins were investigated by means of Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). Noteworthy, it has been found that proteins are adsorbed in a very different way with respect to the bare semiconducting P3HT. Indeed, both the adsorption kinetics and the adsorbed mass are specific for each different extracellular matrix proteins. These results pave the way to the unravelling of the role of the electrical properties of substrates on the interaction with biological moieties.

PO036

Synthesis and characterization of the $Sm_y(Fe_xNi_{1-x})4Sb_{12-\delta}Sn_\delta$ filled skutterudite for thermoelectric applications

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Filled skutterudites form a fascinating class of intermetallic materials with general formula $RE_yM_4Sb_{12}$ (RE = rare earth, M = transition metal). If properly designed, they have important thermoelectric properties that can be modulated through the insertion of RE atoms filling the available voids within the structure.

Starting from the already characterized structure of $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ [1], Sb was partially replaced by Sn in the attempt to create new scattering centers, and therefore further lower the phonon thermal conductivity. The new skutterudite under investigation has the following stoichiometry: $Sm_y(Fe_xNi_{1-x})_4Sb_{11.5}Sn_{0.5}$.
A preliminary study was performed in order to determine the amount of Sm actually entering the structure. The Skutterudite was then synthesized by the conventional melting-quenching-annealing technique starting from Fe, Ni, Sn, Sb and the precursor $Sm_{0.15}Sb_{0.85}$. Ten compositions belonging to the $Sm_y(Fe_xNi_{1-x})_4Sb_{11.5}Sn_{0.5}$ system ($0.40 \leq x \leq 1.00$; $0.18 \leq y \leq 0.55$) were prepared. Structure and composition of the so obtained materials were studied by light optical microscopy (LOM), scanning electron microscopy (SEM), X-ray powder diffraction (XRPD). Structural models were optimized using the Rietveld technique. Differential thermal analyses (DSC) were also performed and the results were compared to the ones obtained from the Sn-free system [3,4].

[1] Artini, C., Zanicchi, G., Costa, G.A., Carnasciali, M.M., Fanciulli, C., Carlini, R. Correlations between structural and electronic properties in the filled skutterudite $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$, Inorg. Chem. 55 (2016) 2574-2583.
[2] Artini, C., Fanciulli, C., Zanicchi, G., Costa, G.A., Carlini, R. Thermal expansion and high temperature structural features of the filled skutterudite $Sm_\beta(Fe_\alpha Ni_{1-\alpha})_4Sb_{12}$, Intermetallics 87 (2017) 31-37.
[3] Artini, C., Parodi, N., Latronico, G., Carlini, R. Formation and decomposition process of the filled skutterudite $Sm_y(Fe_xNi_{1-x})_4Sb_{12}$ ($0.40 \leq x \leq 1$) as revealed by differential thermal analysis, J. Mater. Eng. Perform 27 (2018) 6259-6265.
[4] G. Latronico, P. Mele, C. Artini, P. Manfrinetti, S. W. Pan, Y. Kawamura, C. Sekine, Saurabh Singh, T. Takeuchi, T. Baba, C. Bourgès and T. Mori. Investigation on the Power Factor of Skutterudite Smy(FexNi1-x)4Sb12 Thin Films: Effects of Deposition and Annealing Temperature, Materials 14 (2021) 5773 (1-15).

PO037

A μ-Raman study of complex doped ceria systems at the liquid nitrogen temperature

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RE-doped ceria systems (RE= trivalent rare earth) are able to conduct O^{2-} ions between 673 and 973 K, thus being possible electrolytes for Solid Oxide Fuel and Electrolysis Cells working in the intermediate temperature range (IT-SOFCs and IT-SOECs, respectively). In $Ce_{1-x}RE_xO_{2-x/2}$ systems, the ionic conductivity is given by the oxide structure, which is strongly influenced by the nature and the amount of the RE employed [1]. In general, the highest ionic conductivity is observed for x≤0.20, in a compositional region where the systems show the fluorite-type structure of pure ceria, a fraction of Ce^{4+} ions is randomly replaced by RE, and oxygen vacancies formed to maintain the charge neutrality are free to move through the lattice. However, defect aggregates in the structure can hinder the vacancies movement, reducing the ionic conductivity of the oxide: an in-depth structural characterization is therefore essential to evaluate the behavior of these systems in fuel cells.
Since ceria doped using different RE in combination generally shows improved ionic conductivity properties, our research group synthesized and characterized [2, 3, 4] the $Ce_{1-x}(Nd_{0.74}Tm_{0.26})_xO_{2-x/2}$ and the $Ce_{1-x}(Nd_{0.63}Dy_{0.37})_xO_{2-x/2}$ systems, in which the RE average ionic radii reproduce that of Sm^{3+}, the singly-doped system that shows the highest ionic conductivity. Since μ-Raman spectroscopy plays a key-role in the detection of defects in doped ceria structure, due to its higher sensitivity as a local technique, the spectra of the samples with 0.1≤x≤0.6 belonging to the cited systems were collected at the liquid nitrogen temperature (80 K), to further increase their resolution. This allowed to detect additional defect-related Raman modes that are not clearly observable at ambient temperature, being partially covered by the main signals: all the results from low temperature Raman measurements will be discussed.

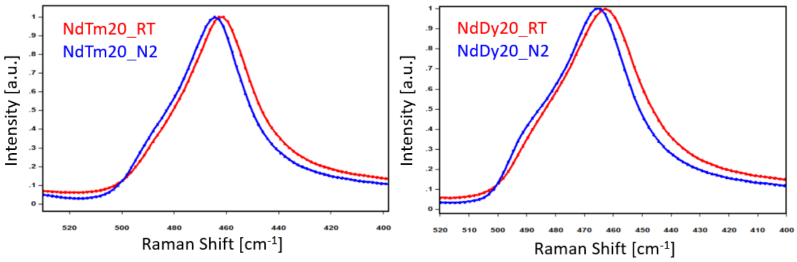

Figure 1: evolution of the profile of the main Raman active mode in Nd/Tm- and Nd/Dy-doped samples with x= 0.20, from 298 K (RT, red) to 80 K (N2, blue).

[1] C. Artini Inorg. Chem., 57 (21) (2018) 13047
[2] C. Artini et al., J. Energy Chem., 60 (2021) 494
[3] C. Artini et al., Inorganics, 7 (2019) 94
[4] C. Artini et al., Inorg. Chem. 60 (2021) 7306

PO038

Innovative hybrid Anion Exchange Membranes for Fuel Cell and Water Electrolysis: Ions Transport Properties and Carbonation Process

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Anion-exchange membranes (AEMs) have received increased interest in recent years as the electrolyte separator in different electrochemical energy conversion and storage (EECS) devices. [1] AEM fuel cells and electrolyzers devices can reach the performance level required by applications with electrocatalysts that do not require a high loading of platinum-group metals (PGMs) due to the alkaline environment at the electrodes. However, the AEM based EECS development and implementation is significantly hindered by the anion exchange membrane (AEM) stability during cell operation, their low OH- conductivity and the low kinetics of the electrocatalysts. In fact, the electrolytic anion-exchange membrane (AEM) is a crucial component which should allow good charge and water transport, i.e. high ionic conductivity, but should also guarantee good chemical, thermal and mechanical stability and high durability. [2]

In this work, nanocomposite AEMs based on Polysulfone ionomer (PSU) and Layered Double Hydroxide (LDH) as nanofiller is reported. [3] PSU is a thermoplastic polymer with high thermal stability, good chemical resistance and mechanical properties. LDHs are mineral anionic clays with elevated ion exchange capacity (IEC). They consist of the positively charged metal hydroxide layers with anions located in the interlayer space. This allows strong hydration of the material together with a large number of hydroxyls on the host layers forming a dense network of hydrogen bonds along the two-dimensional surface, therefore facilitating OH- ion conduction by diffusion mechanism. PSU/LDH AEMs were investigated in both OH^- and HCO_3^- forms, comparing swelling capacity, ionic conductivity and water diffusion. The latter was studied by NMR spectroscopy, measuring the self-diffusion coefficient by the Pulse Field Gradient (PFG) NMR techniques. The nanocomposite membranes are able to maintain good hydration at high temperatures, and to create an adequate nanostructure with the polymer chains, which favour the Grotthuss diffusion mechanism for the OH- ions. Such feature is reflected in the ionic conductivity and in the alkali stability, where they demonstrated the highest conductivity and a reduced membrane degradation rate. In addition, the ^{13}C-NMR technique was used to investigate carbonation processes in the presence of CO_2, showing that the presence of the LDH platelets into the AEM remarkably reduces the conversion rate of hydroxyl groups, as much as slow down the diffusion of carbonate ions. Finally, electrolysis cell tests were conducted on MEAs based on these hybrid membranes, and preliminary results showed very promising performance.

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[1] Vincent, I. and Bessarabov, D. Renewable and Sustainable Energy Reviews (2018) 81, 1690–704.
[2] C.G. Arges, L. Zhang, ACS Appl. Energy Mater. (2018) 1, 2991–3012,
[3] Simari, C. and Nicotera, I. Electrochimica Acta (2022) 403, p. 139713.

PO039

Stability against proteases of GE11 peptide analogues on gold nanostructures

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Among many targeting ligands, peptides have emerged for cell targeting of nanomaterials in diagnostic and therapeutic applications. This is because they can be synthesized at relative low costs, show scarce immunogenity and, being introduced in multiple copies on the nanosystems, provide high affinity for the target. Unfortunately, their application *in vivo* is strongly hampered by their sensitivity to proteolysis. In the present work we show that when peptides are presented on gold nanostructures their stability against proteases is strongly improved without affecting their targeting activity.

Gold nanostructures were assembled from naked gold nanoparticles obtained by Laser Ablation in Solution Technique and were decorated with GE11, a dodecapeptide already known in literature as ligand of the EGF Receptor, which is overexpressed in many tumours of epithelial origin. By linking the targeting motif directly to the gold surface or through a long PEG chain, two kinds of nanosystems showing different peptide density and exposure were thus obtained [1]. In the presence of serine proteases or 20% human serum, we observed that the isolated targeting peptides were rapidly digested. On the contrary, no proteolytic fragments were detected during incubation of the nanosystems and after 24 h digestion. Moreover, the nanostructures preserved their targeting activity and selectivity on colonrectal cancer cells overexpressing or not the EGFR. Molecular dynamic calculations of the interaction between the chymotrypsin serine proteases and the nanosystems allowed us to elucidate the motive of the targeting peptide preservation against the enzymatic digestion. Namely, we found that the formation of the peptide-enzyme complex, which is the firt step of the degradation process, is inhibited by the hindrance imposed to the peptide by its anchoring to the gold surface. These results support the employment of peptides as active targeting units in nanomedicine [2].

[1] F.Biscaglia, S.Rajendran, P.Conflitti, C.Benna, R.Sommaggio, L.Litti, S.Mocellin, G.Bocchinfuso, A.Rosato, A.Palleschi, D.Nitti, M.Gobbo and M.Meneghetti, Adv.Healthcare Mater (2017), 1700596
[2] F.Biscaglia, I.Caligiuri, F.Rizzolio, G.Ripani, A.Palleschi, M.Meneghetti and M.Gobbo, Nanoscale (2021), 13, 10544

PO040

Adapting liposomes for oral delivery of hydroxytyrosol and curcumin: their fate during a simulated in vitro digestion

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Curcumin and hydroxytyrosol are natural compounds, deriving respectively from the rhizome of *Curcuma Long* and olive oil. By virtue of their established antioxidant properties, they can be proposed as food supplements in a diet poor in these active ingredients [1]. However, they suffer from scarce bioavailability and low stability in biological fluids, therefore, after the ingestion, they do not succeed in effectively reaching the colon and explicating their antioxidant activity. In this study, we encapsulated hydroxytyrosol and curcumin into double polymer-stabilized liposomes, in order to propose them for nutraceutical purposes

Curcumin is highly hydrophobic, so it can be accommodated into the lipidic bilayer of the liposomes, while hydroxytyrosol is water-soluble and can be loaded into their aqueous core. Since liposomes suffer from physical instability, short in vivo circulation lifetime, and uncontrolled release properties, they were functionalized with a double polymeric shell in order to obtain an efficient gastrointestinal delivery. They were first grafted with a layer of polyethylene glycol (PEG), which increases the lifetime of the vesicles and confers them muco-penetrating features [2]. Then they were entrapped into a shell of EudragitS100®, a gastro-resistant polymer with a pH-dependent solubility, by using a pH-driven and organic solvent-free process [3].

The prepared liposomes were characterized in terms of loading capacity and encapsulation efficiency of the chosen compounds, size, and morphology. Then, their antioxidant activity was confirmed through an *in vitro* decolourization assay. Finally, *in vitro* digestion experiments proved that double-shell coated liposomes possess better performance in oral delivery applications compared to naked liposomes. In particular, EudragitS100 is demonstrated to protect the vesicles during the mouth and gastric phases of the digestion, characterized by $pH < 7$ conditions, and then release them during the intestinal phase at neutral-alkaline pH conditions. While the presence of PEG was revealed to be particularly useful during the intestinal phase, since it seems to protect the liposomes from the micellization process and could allow an uptake of whole liposomes.

[1] F. Cuomo et al.molecules. 27 (2022) 3:921
[2] H. He et al. Acta pharmaceutica Sinica. B 9 (2019) 36-48.
[3] De Leo et al. Molecules 23 (2018) 4:739

PO041

Harvesting triplet excitons in TADF emitters with negative singlet-triplet gap: The path towards highly efficient OLEDs

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Organic light-emitting diodes (OLEDs) are already widely available and typically used in television and mobile screens. Nevertheless, their technology is still not optimal and an improvement of their efficiency would have huge economic impact, leading to an important reduction in consumption. Indeed, most of the efforts are focused on boosting OLEDs internal efficiency by optimal harvesting of (non-emissive) triplet excitons. To this end, a possible strategy is based on the phenomenon called Thermally Activated Delayed Fluorescence (TADF) [1-4]. The crucial requirement for TADF emitters is a small singlet-triplet gap EST that enables a thermally driven reverse intersystem crossing (RISC) from the triplet to the singlet manifolds and subsequent fluorescence. While EST is typically positive, recent experimental [5] and theoretical [6,7] studies have shown that several N-doped triangle-shaped organic molecules have the first excited singlet state lower in energy than the first triplet state. This inversion of states has been proposed as a pathway to greatly improve RISC rate, thus leading to optimal TADF emitters. From a theoretical point of view, commonly used quantum chemistry excited state methods, like TDDFT, miserably fails in describing negative EST [6,7]. In this contribution, we present an exploratory study of the energy ordering within the excited singlet and triplet manifolds of different azine and heptazine derivatives described in terms of the fully correlated Pariser-Parr-Pople (PPP) model.

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[1] Endo, A. et al. Adv. Mater. 21 (2009) 4802-4806
[2] Endo, A. et al. Appl. Phys. Lett. 98 (2011) 083302
[3] Dhali, R. et al. Phys. Chem. Chem. Phys. 23 (2021) 378-387
[4] Dhali, R. et al. J. Chem. Phys. 154 (2021) 134112
[5] Miyajima, D. et al. Phys. Sci. (2021) DOI: 10.21203/rs.3.rs-478258/v1
[6] Ehrmaier, J. et al. J. Phys. Chem. A 123 (2019) 8099-8108
[7] de Silva, P. J. Phys. Chem. Lett. 10 (2019) 5674-5679

PO042

Quantum Molecular Dynamics in Out of Equilibrium Environments: Redfield-Smoluchowski and Hydrodynamic Approaches

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The description of quantum molecular dynamics as influenced by a polarizable and dynamically evolving environment is critical to understand the nature of various physical processes, from solvation phenomena to photobiological processes in protein environments, and transport of charge carriers and excitons in nanostructures. However, the typically used dielectric continuum picture for the environment [1,2] is likely to fail when dealing with nonequilibrium solvation effects. On the other hand, fully atomistic first principles quantum calculations are hardly feasible due to the large number of environmental degrees of freedom.

Against this background, we present the effect of a dynamic polar environment on a time-evolving molecular system, using two different approaches, namely the Multistate Redfield-Smoluchowski Equation (MRSE) [3] and the Quantum-Classical Reduced Hydrodynamic (QCRH) approach [4-6]. Both approaches can describe molecular relaxation in condensed dynamic phases, complementing typically used dielectric continuum models for the environment.

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[1] J. Tomasi, B. Mennucci, R. Cammi Chem. Rev. 105 (2005) 2999-3094
[2] A. Klamt, G. Schüürmann, J. Chem. Soc., Perkin Trans. 2 (1993) 799-805
[3] F. Di Maiolo, A. Painelli Phys. Chem. Chem. Phys. 22 (2020) 1061-1068
[4] I. Burghardt, B. Bagchi, Chem. Phys. 329 (2006) 343-356
[5] K. Hughes et al. J. Chem. Phys. 136 (2012) 014102
[6] F. Di Maiolo, I. Burghardt (2022) in preparation

PO043

Carbon Quantum Dots for secure intrabody communication among implantable medical devices

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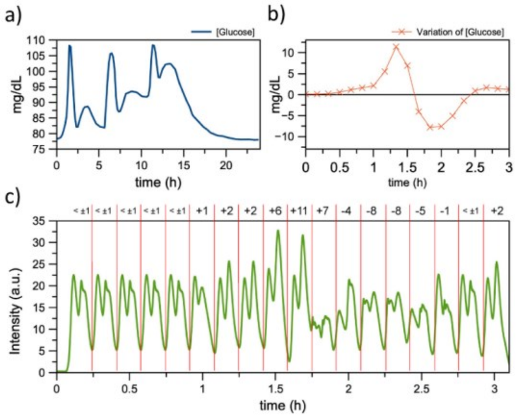
In recent years, there has been an increase in research focused on the study and application of alternative communication methods to traditional ones that enable the exchange of information between bio-implantable medical devices. The latter, which are intended to monitor certain vital parameters or allow the dosing and subsequent release of a drug in an automated manner, require communication that is not based on electromagnetic waves and that at the same time guarantees security, speed, and resistance to possible fraudulent attacks. One possible solution to this issue is Molecular Communication (MoCo), a bio-inspired approach that enables the exchange of information by means of chemical messengers within fluids. [1] The way information is exchanged is very simple: a transmitter encodes the message by releasing small amounts of chemical messengers into the fluid that travels to the receiver, which allows the message to be decoded. In this work, an innovative signal modulation method is presented, both theoretically and experimentally, based on the instability effect caused by a peculiar interfacial phenomenon occurring between two miscible liquids with different viscosity or density in contact with each other. We have called the modulation "Interfacial Shift Keying" (ISK). [2] The chemical messengers used for the experimental campaign are Carbon Quantum Dots (CQDs), which are extremely fluorescent carbon nanoparticles tolerated by the human body due to non-cytotoxicity. Using these information nanoparticles and ISK modulation, we were able to create a prototype of High-Density Information MoCo that simulates the arrangement of a bionic pancreas and to communicate blood glucose variations in the hours following the three main meals of a day. The decoding of the message by the receiver was made possible by using machine learning methods.



[1] N. Tuccitto et al. *Phys. Chem. Chem. Phys.*, 2018, 20, 30312-30320.
[2] F. Calì et al. Carbon 190 (2022) 262-275.

PO044

Bioinspired nanostructured pesticide formulations: eco-sustainable strategies for agriculture

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To combine the compelling environmental concerns with the food needs of the increasing world population, innovative and advanced agricultural techniques are urgently required. Bioactive metabolites spontaneously produced by plants represent natural alternatives to synthetic pesticides. Their large-scale exploitation poses the problem of the rational design of functional chemical formulations. Nanotechnology offers the opportunity to lower the indiscriminate use of pesticides, providing controlled release kinetics, enhanced solubility, stability and permeability [1].

The focus of the scientific activity presented in this contribution is on nanostructured surfactant formulations including natural biopesticides extracted from common spontaneous plants grown on the coasts of southern Italy.

The investigated biopesticides are diacetyl-lycorine, ungeremine, α-costic acid and inuloxin A. Lycorine, a pyrrolo dephananthiridine ring-type alkaloid extracted from different *Amarillydacee*, inhibits the growth and cell division in higher plants, algae and yeasts. Ungeremine is a betaine-type alkaloid obtained from *Pancratium maritimum*, presents a relevant antibacterial activity. α -costic acid, a sesquiterpene obtained from a perennial autochthon shrub, *Dittrichia viscose*, is an effective acaricidal. Inuloxin A, a sesquiterpene extracted from *Inula viscosa*, is endowed with a high potential in the management of parasitic plants [2-6].

The allow the delivery of these bioactives, micellar systems formed by several types of surfactants were tested, including the anionic surfactants sodium dodecyl sulphate (SDS) and sodium laurylether sulphate (SLES), the cationic surfactant cetyltrimethylammonium chloride (CTAC) and the nonionic 20-polysorbate (tween 20). UV-spectroscopy was used to evaluate the pesticide inclusion in the micelles, while dynamic light scattering revealed the changes in the micellar dimension upon biopesticide inclusion. Analysis of the results allowed the identification of the surfactant features necessary to obtain functional formulations.

As the final part of the work, we present preliminary results on the possible exploitation of rhamnolipids, as solubilizing agents. Rhamnolipids are of glycolipids produced by *Pseudomonas aeruginosa* which are arousing an increased interest as possible substitutes of synthetic surfactants [6]. The combination of biopesticides and biosurfactants opens new avenues to bioinspired formulations for sustainable agricultural practices.

[1] S. Kumar et al. J. Control. Release 294 (2019) 131
[2] K.K. Scharder et al. J. Agric. Food Chem. 61 (2013) 1179
[3] A. Cimmino et al. Nat. Prod. Res. 35 (2019) 1428
[4] D. Lamoral-Theys at al. J. Med.Chem. 52 (2009) 6244
[5] A. Moeini et al. Carbohydr. Polym. 230 (2020) 115627
[6] A. Andolfi et al. Phytochemistry 86 (2013) 112

Use of carbon-based nanodots as fluorescent probes in pH sensors: direct monitoring of bacterial growth

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Quantum dots are well-known fluorophores used in many applications due to their high photostability and brightness. Among them, carbon quantum dots (CQDs) are a relatively new class of carbon nanomaterials which have been extensively studied in the last years to improve their properties towards the final application [1]. Nowadays, most common approaches for CQDs production span from laser ablation, microwave-mediated synthesis, hydro-/solvo-thermal methods and pyrolysis [2]. Here we propose an innovative one-pot synthesis to obtain pH-sensitive CQDs with tunable fluorescence properties. In particular, the procedure is based on the pyrolysis of citric acid (CA) in the presence of different amino acids (i.e., phenylalanine, Phe, or tryptophan, Try). The synthesis has been optimized in terms of decomposition time and dopant concentration to tune the response to pH. Obtained CQDs result sensitive to very small changes in the pH of the aqueous environment thanks to remarkable variations of their fluorescence. Our results evidence that in the CA/Phe case the fluorescence decreases as the pH decreases with an inflection point at pH 6.6, while the system prepared with Try shows an opposite behaviour with an inflection point shifting at higher pH (i.e. 8.3). This different optical response can be addressed to the different functional groups localised at the surface of the CQDs. These carbon-based nanostructures have been tested, in vitro, for the evaluation of the susceptibility of E. coli ATCC 25922 to ampicillin and eventually to estimate the Minimal Inhibitory Concentration (M.I.C.).

[1] K. J. Mintz et al. Nanoscale 11 (2019) 4634
[2] Wang, Ru, et al. Journal of Materials Chemistry A 5 (2017) 3717
[3] D. Yongqiang, et al. Carbon 50 (2012) 4738

PO046

Rationalizing Sequence and Conformational effects on the guanine oxidation in different DNA conformations

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The effect of the environment on the guanine redox potential is studied by means of a theoretical-computational approach, the Perturbed Matrix Method (PMM)[1]. The PMM allows to describe the molecular electronic properties in complex systems through a mechanical-statistical treatment from which it is possible to extract thermodynamic properties, such as free energy.
Our data, in agreement with previous experimental findings[2], clearly show that the presence of consecutive guanine bases in both single and double stranded DNA oligomers lowers their reduction potential. Such an effect is even more marked when a G-rich quadruplex (G4) is considered, where the oxidized form of guanine is particularly stabilized. To the best of our knowledge, this is the first computational study reporting on a quantitative estimate of the dependence of the guanine redox potential with respect to sequence and conformational effects in complex DNA molecules, ranging from single-stranded DNA to G-quadruplex in aqueous solution.

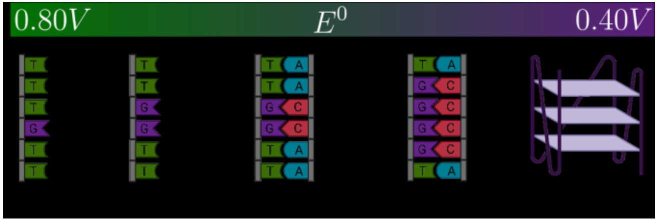

Figure 1. Colorbar of the calculated reduction potentials (E^0, vs SHE) of the indicated substrates in solution.

System	*T(K)*	*E^0(V)^a PMM*	*Δ(V) PMM*	*Δ(V) exp.^{2}*
ss-HG1	278	0.80	0.00	0.00
ss-HG2	278	0.69	0.11	0.10
ss-HG2	300	0.83	-0.03	0.00
ds-HG2	278	0.69	0.11	0.11
ds-HG4	278	0.55	0.25	0.20
G4	278	0.40	-	-

The one electron reduction potentials of oxidized guanine in single and double strands, with increasing number of adjacent guanine bases in a fully solvated environment are reported in Table 1. We reproduced quantitatively the experimental reduction potential shift (*Δ*) of each investigated system with respect to the reference compound ss-HG1.

Table 1. Calculated reduction potential (E^0, vs SHE) of oxidized guanine in each substrate, calculated and experimental potential shift (*Δ*). ^{a}The estimated standard error is ± 0.04 *V*.

[1] L. Zanetti-Polzi et al. Phys. Chem. Chem. Phys. 20 (2018) 24369.
[2] A. Capobianco et al. J. Phys. Chem. B. 119 (2015) 5462.

Chemically cross-linked gelatin hydrogels: glutaraldehyde and glyceraldehyde effect on structural, diffusional and mechanical properties

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Hydrogels have received great attention owing to their high-water content, tunable properties, and similarity to natural tissues, which make them suitable for being used as tissue engineering scaffolds [1] or drug delivery systems [2]. The possibility to customize solute diffusion, mechanical and degradation properties modulating the cross-lining degree is of utmost importance for hydrogels applicability. Gelatin is a protein-based natural polymer, derived from the hydrolysis of collagen. Owing to its biological origin, it represents an excellent candidate for the preparation of biocompatible hydrogels, even if a cross-linking treatment is required to prevent its dissolution at physiological temperature. To overcome cytotoxicity problems raised by the use of glutaraldehyde, a conventional gelatin cross-linker, glutaraldehyde has been proposed as a more biocompatible alternative [3]. In this work, we investigated the effect of different cross-linking reaction conditions on the physico-chemical properties of gelatin hydrogels. Samples were cross-linked with glutaraldehyde and glyceraldehyde systematically varying the concentration of cross-linkers, acetone, and water. The cross-linking degree, estimated from 2,4,6-Trinitrobenzene Sulfonic Acid (TNBSA) assay, and the dissolution behavior at physiological temperature were investigated, showing that the reaction conditions strongly affect hydrogels stability against dissolution at 37 °C. The morphology and porosity of the corresponding xerogels were analyzed by means of scanning electron microscopy (SEM), whereas X-rays scattering was used to clarify the cross-linking effect on the gel network at the nanoscale. The mechanical and diffusional properties of gelatin cross-linked hydrogels were correlated with the cross-linking degree: compressive strength of gelatin hydrogels is strongly dependent on the cross-linking degree and on the type of cross-linker, whereas the diffusion coefficient of a model drug, namely methylene blue, thought the hydrogel is not affected by the chemical modifications.

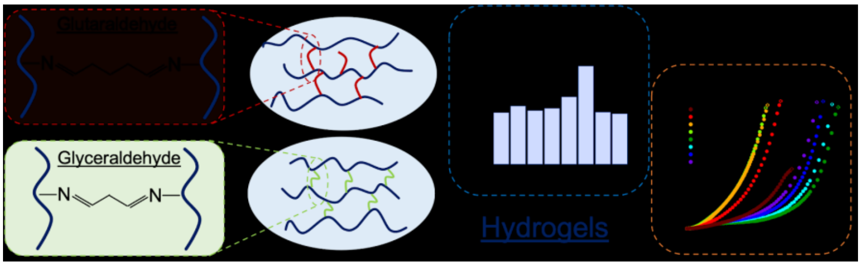

Figure. Graphical abstract of the work.

[1] G.D. Nicodemus et al. Tissue Eng. Part B Rev. 14 (2008) 149-165
[2] J. Li et al. Nat. Rev. Mater 1 (2016) 1-17
[3] M. A. Vandelli Int. J. Pharm. 215 (2001) 175-184

PO048

Cross-linked porous gelatin microparticles with tunable shape, size and porosity

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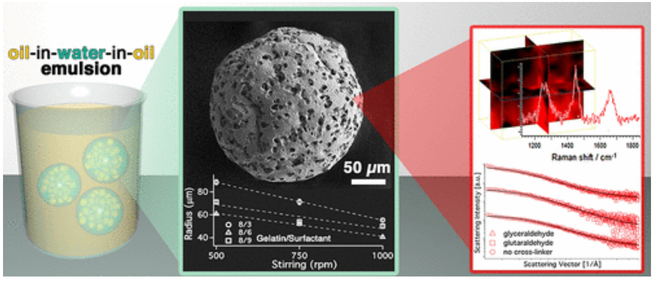
Polymeric microparticles are relevant to many applications in the biomedical field including drug delivery, tissue engineering, and for the preparation of microscaffolds for cell culture. Gelatin is particularly attractive in this context due to its excellent biocompatibility, availability, and versatility, even if its use at physiological temperature requires a cross-linking process to prevent dissolution [1]. Gelatin microparticles can be obtained by means of a variety of methods such as spray drying, precipitation, solvent evaporation, and emulsification: the latter approach, when double emulsions are exploited, allows one to achieve microporous particles with different architectures [2]. This is of paramount importance since controlling the shape, size, porosity, swelling, and stability against dissolution is fundamental toward microparticles application in physiological conditions.

In this contribution we describe the preparation of porous gelatin microparticles by means of oil-in-water-in-oil (O/W/O) emulsions, modifying the synthetic parameters such as gelatin/surfactant ratio and the stirring speed [3]. The effect on the structural properties, including surface and inner porosities, was assessed by multiple microscopy techniques (optical, electron, and confocal Raman). Selected samples were then cross-linked with glutaraldehyde or glyceraldehyde, and their swelling properties and stability against dissolution were evaluated, while the influence of the cross-linking at the nanoscale was studied by scattering of X-rays. Depending on the preparation protocol, we obtained particles with different shapes (irregular or spherical), radii within ~40 to 90 µm, and porosities up to 10 µm. The cross-linking prolongs the stability in water from a few minutes up to several days whereas the swelling ability and the mesh size at the nanoscale of the gelatin network are preserved. The analysis of the experimental results as a function of the preparation parameters demonstrates the possibility to design microparticles with tunable features.



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[1] C.E. Campiglio et al. Materials 12 (2019) 2476
[2] K. Nilsson et al. Bio-Technology 4 (1986) 989-990
[3] R. Gelli et al. Langmuir 37(44) (2021) 12781-12789

PO049

Investigation of Cu-based nails of Punic Ship of Marsala

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During the organization of the new exhibition of Museo Lilibeo, inaugurated in March 2017, numerous metal finds, belonging to the wreck of the Punic ship, were rediscovered in the deposits. These are very important elements for understanding the ship's construction method and, for this reason, a showcase has been dedicated to them, which is one of the most admired in the exhibition. The batch of finds consists of lead sheets used for the hull lining below the waterline and of several countless pegs and residual heads used for fixing the above sheets, of long and folded nails used to ensure the frames of the hull to the planking, of wooden dowels having nails inside them and of concretions of iron nails.

One of the questions asked by the archaeologists themselves at the time of the exhibition concerned the composition of the alloys. In the literature, the nails are defined tout court as "copper nails", but the detailed excavation report, published by Honor Frost, addresses the question in a critical and scientifically way, and deserves further investigation [1]. Then, the other questions concern the unusual corrosion, evident in the nails and in the lead sheets, and with a big variability of thickness and colours of patina and concretions.

Here, the non invasive investigation of 30 nails and 3 fragments of lead sheathing, belonging to the wreck of the Punic ship, is reported. Portable X-ray Fluorescence (XRF) and Raman Spectrometer allowed us to identify the elements and compounds constituting them making some discussion deductions about their composition. X-ray diffractometry and optical microscopy of a cross section permit to explain the degradation occurred in the underwater environment.

[1] Frost H. et alii, Lilybaeum (Marsala) The Punic Ship Final Excavation Report, Notizie degli Scavi di Antichità XXX (1976), suppl. 1981, pp. 119-125.

PO050

Optimizing the electrochemical performances of $Na_3MnZr(PO_4)_3$ and $Na_3MnTi(PO_4)_3$ cathodes for SIBs: the role of conductive carbon amount in tape-casting and self-standing electrodes

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Among the cathode materials for SIBs, $Na_3MnZr(PO_4)_3$ [1] and $Na_3MnTi(PO_4)_3$ [2] are very attractive and promising, as they have high working voltage and do not contain toxic elements. Anyway, as for the other cathode materials, they suffer for low electronic conductivity, expansion of volume structure during charge/discharge cycles and $Na_3MnZr(PO_4)_3$ has a low theoretical capacity (107 mAh/g); some limits can be overcome by carbon-coating the active material during synthesis, and by choosing the proper carbon source and amount. In this frame, we made a systematic study of the conductive carbon contribution to the electrochemical performances of the two phosphates. At first, we focused the research on the electrodes prepared by tape-casting. We synthesized the two cathode materials $Na_3MnZr(PO_4)_3$ [1] and $Na_3MnTi(PO_4)_3$ [2] via sol-gel, using different quantity of citric acid as carbon source for coating. We tested three different amounts of citric acid, given as citric acid/compounds molar ratio: 8.8, 3, and 2. The physical and chemical features of the carbon coated on the active material surface was characterized by several techniques: X-Ray diffraction, SEM-EDS and TEM, RAMAN spectroscopy, TGA. The slurries compositions were: a) 70% of $Na_3MnZr(PO_4)_3$, 20% of Acetylene black, 10% of PVdF; b) 70% of $Na_3MnTi(PO_4)_3$, 20% of Super-P, 10% of PVdF. Cyclic voltammetry and charge/discharge cycles at different C-rates demonstrate the best performances for both samples are obtained by citric acid/compound molar ratio of 2.

Secondly we implemented the two cathodes $Na_3MnZr(PO_4)_3$ and $Na_3MnTi(PO_4)_3$ with the most performing carbon coating into self-standing electrodes using electrospinning technique [3]. We electrospinned a polymeric matrix containing the cathodic active material [3]. The matrix is stabilized in air and carbonized in Nitrogen atmosphere in order to graphitize the polymeric component and obtain an extremely electronic conductive electrode. The prepared self-standing electrode is characterized with X-Ray diffraction, SEM and TEM microscope, Raman spectroscopy, TGA analysis, cyclic voltammetry, and charge/discharge cycles at different C-rates. We conclude that the active material is dispersed homogenously among the CNFs and into them, the stabilization and carbonization processes give us a quite graphitized CNFs and finally the self-standing preparation guarantees a quite good performance also at high C-rate such as 20C, greater than slurry electrodes that at 5C have already a very low capacity.

[1] H. Gao et al. J. Am. Chem. Soc. 140 (2018) 18192
[2] Y. Zhou. et al. ACS Appl. Mater. Interfaces 12 (2020) 30328
[3] G. Meligrana et al. ChemElectroChem 7 (2020) 1652

PO051

Self-standing electrospinned carbon nanofibers anodes: influence of carbonization temperature on the electrochemical performances

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Carbon nanofibers are achieving growing interest as anode materials for LIBs [1,2] and SIBs [2,3], as they meet some paramount requirements, such as electronic conductivity, flexibility to control the volume expansion of active material [4], ultra-long lifespan [5] and good performance at high C-rate [6], for optimized performances. Among the methods used to prepare CNFs anodes, the electrospinning reveals a simple, scalable and versatile technique [7]. Notwithstanding the grown interests in electrospinned electrodes, a systematic study i) investigating the influence of the experimental conditions used to spin, stabilized and graphitized CNFs, ii) evaluating the physical and chemical properties of CNFs at different carbonization conditions and iii) relating them to CNFs electrochemical performances, is still lacking. These aspects are not trivial, also in the light to apply electrospinning to prepare self-standing electrodes containing the active material dispersed into the CNFs matrix [8].

In this frame, we decided to prepare self-standing carbon nanofibers (CNFs) altering carbonization temperature in order to study the change of morphology and nanofiber diameter, electronic conductivity and the CNFs cathodic and anodic performances. The CNFs are synthesized by solubilizing Polyacrylonitrile polymer (PAN) in Dimethylacetamide (DMAc) [8], and then using electrospinning technique to obtain the final electrode. The CNFs are analyzed using X-Ray diffraction, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), RAMAN spectroscopy, and impedance spectroscopy. From these analyses we conclude that the temperature influences the dimension of CNF diameter, electrode thickness and electronic conductivity: increasing the temperature from 600°C to 900°C the diameter and thickness decrease instead the electronic conductivity gets better. Moreover, the best carbonization temperature is used to prepare CNFs to be applied as anode for SIBs and LIBs. In this last step the anodes are tested with cyclic voltammetry and charge/discharge cycles. The CNFs anode is electrochemically active for SIBs and LIBs, and in both cases the anode gives quite good results also at high C-rate such as 20C.

[1] C. Kim et al. Adv. Funct. Mater. 16 (2006) 2393
[2] J.W. Jung et al. J. Mater. Chem. A 4 (2016) 703
[3] W. Li et al. Nanoscale 6 (2014) 693
[4] R. Chen et al. J. Mater. Chem. A 5 (2017) 12914
[5] Y. Wu at al. ACS Appl. Mater. Interfaces 5 (2013) 12175
[6] S. Yu et al. J. Mater. Chem. A 6 (2018) 18304
[7] L. Persano et al. Macromolecular Materials and Engineering 298 (2013) 504
[8] G. Meligrana et al. ChemElectroChem 7 (2020) 1652

PO052

Optimizing the electrochemical performances of ZnS anodes for SIBs

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In a society heavily based on the use of electric energy as ours, batteries are becoming more and more necessary and are gaining large-scale application. As concerns anodes for LIBs and SIBs, some drawbacks, such as the poor electronic conductivity of the active materials and the volume changes occurring during the Li or Na insertion/de-insertion upon cycling, need to be solved in a short time. Among the approaches used to overcome the anodes limitations, the use of active materials/conducive carbon composites, with different compositions, nanostructures and morphologies, as well as doping are considered the most feasible and simple ones. In this frame, we synthesized, characterized (techniques: XRPD, SEM-EDS, TEM. Raman spectroscopy, TGA) and compared the electrochemical performances of ZnS anodes obtained by two synthesis routes: sol-gel [1] and hydrothermal [2]. From the first approach ZnS/carbon nanoparticles are obtained and from the second one ZnS/reduced graphene oxide nanoparticles are formed. Both materials were tested by cyclic voltammetry and charge/discharge cycles at different C-rate on slurries prepared by tape-casting. The best electrochemical performances were obtained for the ZnS/reduced graphene oxide (150 mAh/g at 2C, about 200 mAh/g after 200 cycles at C/5).

We also investigated the Cu doping (5 and 10% moles); the Cu does not substitute Zn ions in the sphalerite structure, but segregates as CuS (covellite phase), thus forming a composite with improved electrochemical performances.

Finally, we implemented the ZnS/reduced graphene into self-standing electrodes. The active material was dispersed into a polymeric solution (10% wt), subsequently deposited by electrospinning [3]. The obtained electrospinned film was stabilized in air and carbonized in Nitrogen atmosphere in order to graphitize the polymeric component and obtain an extremely electronic conductive electrode. The self-standing electrode was characterized by several techniques (XRPD, SEM-EDS, TEM microscope, Raman spectroscopy, TGA), and tested by cyclic voltammetry and charge/discharge cycles at different C-rates. The preliminary results are encouraging and demonstrate promising electrochemical performances, with high coulombic efficiency (> 99%) over 200 cycles at C/5. As concerns the specific capacity, its values are comparable to those given by the cells prepared by tape-casting, and work is in progress to increase the active material loaded into the carbon nanofiber, to optimize the performances of the electrospinned material.

[1] K. Yang et al. J. Power Sources 402 (2018) 340
[2] W. Qin et al. Electrochim. Acta 191 (2016) 435
[3] G. Meligrana et al. ChemElectroChem 7 (2020) 1652

PO053

The Structural Study of a Eutectic Solvent Reveals Hydrophobic Segregation and Lack of Hydrogen Bonding between the Components

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A DES (deep eutectic solvent) is formed by the judicious combination of a hydrogen bond (H-bond) donor and an acceptor, solid starting materials that melt if put in contact at precise molar ratios. As a result, a liquid mixture is obtained with a melting point that is not only lower than those of the pure constituents, but also than the one predicted by assuming a thermodynamic ideal behaviour of the liquid phase. The driving force of such phenomenon has been long debated and seems usually rely on the strong and extensive H-bond network that is established between the components. The majority of DESs are based on at least one ionic component, and dominated by strong H-bonding compounds. However, the ongoing research on these solvents has very recently led to the introduction of a new class named "type V", formed by non-ionic compounds. As a subclass of type V DESs, hydrophobic DESs (HDESs) have been proposed[1]. They possess significant advantages over common hydrophilic DESs. For example, their ability to form biphasic systems with water makes them more suitable for liquid-liquid extractions and microextractions.

Here, we present our study about a eutectic mixture formed by butylated hydroxytoluene (BHT) and L-menthol (MEN), in 1:3 molar ratio. This eutectic has been very recently developed and has shown outstanding results in liquid-liquid microextractions of pesticides and fat-soluble micronutrients on food samples[2]. Particular accent has been put on the structural arrangement in solution to unveil the interaction that led to the formation of the eutectic solvent. This urgency arises from the observation that the formation of H-bonds by the BHT seems to be dramatically impeded because of the high steric hindrance suffered by its hydroxyl group (Figure 1 a). To this purpose, a combined approach including differential scanning calorimetry (DSC), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, small and wide angle X-ray scattering (SWAXS), and molecular dynamics (MD) simulations has been employed.

The results agree that no hydrogen bond are played by the BHT molecules. This results in a hydrophobic segregation promoting interaction between menthols molecules, even more intense that the pure compound (Figure 1 c).

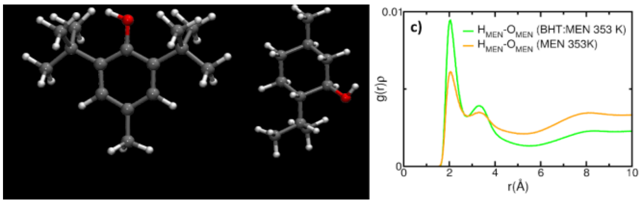

Figure 1. a) Butylated hydroxytoluene, b) L-Menthol, and c) Radial distribution functions multiplied by the numerical densities of the observed atoms for the H_{MEN}-O_{MEN} distribution in the BHT:MEN and pure MEN systems at 353K.

[1] Abranches, Dinis O., et al. *Chem. Commun.* 55.69 (2019) 10253-10256

[2] Chiara Dal Bosco et al. ACS Sustain. Chem. Eng. 9.24 (2021) 8170-8178

PO054

Theoretical models and sensing tools for mapping anthropogenic pollutants in the troposphere using drones

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Nowadays, unmanned aerial vehicles (UAVs), also called drones, are widely used where it is necessary to map large areas. In most cases, they are equipped with cameras, but they are now increasingly used in unconventional applications by equipping UAVs with other sensory devices including chemical detectors. The ability to pair the GPS position of the aircraft with sensor data opens the way to countless environmental applications. In this context, the use of UAVs for the mapping of gaseous substances, possibly pollutants, in the open field is noteworthy. Our research focused on petrochemical industrial plants. At these industrial sites, odor comfort, air composition, and related worker health and safety requirements are of upmost importance. Indeed, at petrochemical plants, refineries, and similar chemical industries, monitoring air composition is a primary health and safety concern. The regulatory authorities require timely investigation of the possible distribution of pollutants before granting production permits. Chemical dispersion models are routinely used for environmental impact assessment, risk analysis, and emergency planning. Therefore, a detailed analysis of the distribution of pollutants is necessary. Unfortunately, chemical plants are characterized by complex 3D distributions of buildings, rack pipes, tanks, distillation columns, etc., resulting in highly challenging substance-analysis operating conditions. We present here a preliminary predictive theoretical investigation of the potential effect of a source of anthropogenic pollutants coupled with an experimental campaign to verify and consolidate the theoretical results. In particular, we focused on the detection of odorous compounds. In this industrial context, the main component is thiols. Our theoretical models predict the need for two detection methods operating at two concentration levels. At high concentrations, typically present near the source (the industrial site), it is necessary to develop detection methods operating in the ppm regime. In this context, we present results obtained with carbon-based fluorescent nanoparticles. The detection mechanism is based on TURN-ON of the fluorescence of carbon dots quenched by copper ions when subjected to bubbling with air polluted by thiols. Precipitation of the copper sulphides turns the luminescence of the nanoparticles back on. Moving away from the source, our theoretical models predict rapid reduction of mercaptan concentrations to concentrations even several orders of magnitude lower, around ppb. Unfortunately, although these concentrations are minimal, the odour thresholds of these compounds are equally low. Therefore, the problem is still perceived in the proximity of receptors in inhabited places near the plants. We present a method for detecting such low concentrations based on determination by time-of-flight secondary ion mass spectrometry (ToF-SIMS). It can detect mercaptan compounds that spontaneously adsorb on noble metal surfaces (Au, Ag, Pt) with high sensitivity reaching the concentrations that theoretical models predict. We eventually propose a solution to minimize the effect of drone turbulence on pollutant mapping based.

PO055

Nanoscale electrical characterization by advanced conductive atomic force microscopy techniques of alpha-Sn nanospheres on silicon

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This work aims at mapping the spatial distribution of surface electrical properties on the nanoscale, by means of advanced conductive AFM techniques, of Sn nanospheres (NS) grown onto silicon substrate. A microwave-based synthetic route for the preparation of tin NS with a diamond-like α-phase structure on silicon was recently demonstrated [1]. The synthesized material shows an extraordinarily narrow direct bandgap (around 50 meV) and an improved thermal stability (up to 200° C). Representing the most innovative features of this synthetic process, microwaves turned out to be instrumental in achieving the specific nanostructures reported.
Besides standard microscopic and structural characterization, to explore the effect of different preparation processes at the nanoscale on the Sn NS and Si substrate, conductive Atomic Force Microscopy (c-AFM) and Kelvin Probe Force Microscopy (KPFM) represent advanced complementary characterization techniques to investigate nano-electrical properties of the material with a spatial resolution of the order of 10 nm or less. By combining morphological investigation with functional electrical mapping, the c-AFM allows to obtain the topography and the electrical conductivity map of the sample by using a conductive tip; KPFM allows to spatially trace the surface potential, i.e. the contact potential difference (V_{CPD}), and to determine the work function (WF) of the sample, knowing the WF of the tip (obtained by measuring a reference sample), thanks to the equation: $eV_{CPD} = WF_{sample} - WF_{tip}$. c-AFM analysis on Sn NS, allowed to detect an increase of the current on top of the Sn particles and a not always linear variation of the current of the order of few pA by applying different bias voltage (from -1 V to +1 V) was observed. Moreover, the spatial distribution of the current appears different on samples subjected to different synthetic processes. In addition to electrical characterization, AFM allows to obtain information on mechanical properties correlated to the different stresses suffered by the material during the synthesis process which therefore leads to different structural properties and electrical responses. Furthermore, nanolithography was incidentally observed, disclosing the possibility to fabricate nanocontacts for specific applications for which this kind of samples seems really promising, such as far infrared photodetectors.

[1] I. Mazzetta et al. Materials & Design 217 (2022) 110632

PO056

Absorption behavior of doxorubicin hydrochloride in Visible region in different environments: a combined experimental and computational sturdy

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Doxorubicin hydrochloride (DX) is an antibiotic molecule belonging to the anthracycline family of anticancer drugs[1]. Both the absorption and emission spectra of DX are quite sensitive to the environment polarity, a feature that can be exploited, for example, to follow the migration of DX from the bulk water phase to micellar aggregates[2]. Therefore, in the present work we combined the experimental absorption measurements in the interval of 350-600 nm (Vis), molecular dynamics simulations, quantum-mechanics calculations and an advanced molecular treatment of simulation data to provide a complete picture of the absorption behavior in the visible portion of the electromagnetic spectrum of the molecule in different solvents. In particular, the Perturbation Matrix Method (PMM)[3,4], a QM/MM approach[5], was used in order to accurately model the conditions of DX in bulk solvent on the timescale of several nanoseconds, in order to properly describe the temporal evolution of the system. By such an approach, we have shown that it is possible to characterize the effect of the environment on the DX absorption behavior - including the vibronic contributions - as well as to interpret such differences in terms of molecular electronic excited states, which are found to be strongly influenced by the environment. The MD-PMM simulations also revealed that in order to correctly reproduce the measured absorption features, the contributions arising from different conformers need to be considered (see Figure).

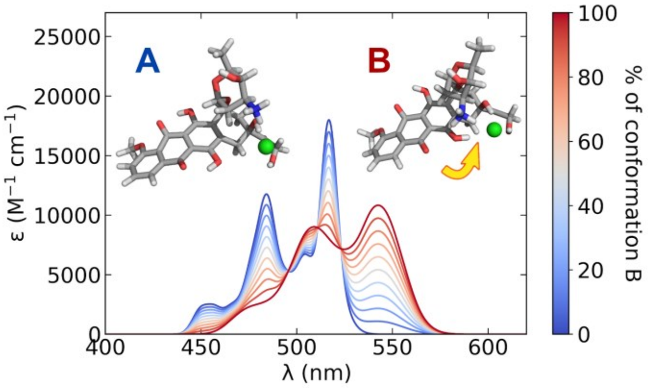

Figure: Predicted absorption spectrum of DX in *n*-hexane at different populations of two conformers (A and B).

[1] E. Ravina, *The evolution of drug discovery: from traditional medicines to modern drugs*, John Wiley & Sons, (2011).
[2] E. Tasca et al. *J. Colloid Interface Sci.* 540 (2019) 593–601.
[3] M. Aschi et al. *Chem. Phys. Lett.* 344 (2001) 374–380.
[4] M. D'Abramo et al. *Chem. Phys.* Lett. 424 (2006) 289–294
[5] E. Brunk, U. Rothlisberger, *Chem. Rev.* 115 (2015) 6217–6263.

PO057

Photoactive nano-junctions based on self-assembled mixed metal-complex molecular wires

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The fabrication of stable and photo-responsive molecular nano-junctions represents a crucial research step towards the development of optoelectronic nano devices. A possible way for accomplishing this goal involves bottom-up approaches based on self assembly strategies. In recent years we have developed methodologies for robust anchoring on solid surfaces of molecular wires with outstanding conductivity properties, based on stepwise assembly of poly terpyridine metal complexes on a variety of surfaces [1-3] [Nature materials, Adv. Materials, Nanoscale], including transparent (semi)conductive substrates. By means of these methodologies it is possible to obtain supramolecular architectures in which different metal ions can be alternated in the desired order for tailoring the optical and electrical properties of the system.

In this contribution we report on the preparation and characterization of terpyridine-based mixed metal complex molecular wires based on different sequences of iron and ruthenium metal centres. The obtained architectures were characterized by means of time-of-flight secondary ion mass spectrometry and optical spectroscopies. Preliminary photo-electrical characterization results, performed by using junctions based on PEDOT/Molecular wires/Gold/Silicon oxide in ad hoc fabricated pattern, indicate that the conductivity of the molecular wires can be modulated by means of an external photo-stimulation and it is depending also on the sequence of redox centers into the molecular wires backbone.

[1] S. Vitale et al. *Nanoscale*, 11 (2019) 4788-4793
[2] C. Musumeci et al. *Advanced Materials* 26(11) (2014) 1688-1693
[3] N. Tuccitto et al. *Nature Mater* 8 (2009) 41-46

PO058

3D nanostructured electrodes for investigating ECL mechanisms

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Electro generated chemiluminescence (ECL) is a light emitting process involving high-energy electron-transfer reactions of electroactive species at the electrode surface. The technique is characterized by a very low background noise, due to the absence of an external light excitation source which makes it particularly convenient for analytical transduction. In such a context, it generally involves simple preparation procedures and high speed of analysis if compared with other analytical techniques having a similar sensitivity. These peculiar features make ECL a very powerful tool for the detection of targets at ultra-low concentration.

Typically, common ECL experimental setups involve a luminophore and an inexpensive co-reactant used in relatively large excess which is, e.g., oxidized at the electrode surface and spontaneously decays to a highly reducing radical intermediate susceptible to react with the luminophore. The reduced form of the luminophore reacts then with the pristine oxidized co-reactant to finally generate an electronically excited state of the original luminophore that produces a radiative emission coming back to the ground state.

Nanoporous materials are characterized by high specific surface area, controllable pore structure and versatile functionality and can be used to build up a three-dimensional electrode matrix for ECL systems. In fact, they can load abundant luminophore per unit of area and can provide a three-dimensional (3D) matrix for accelerated mass and charge transfer processes given that the luminophore can be anchored inside the diffusion layer of the electrochemically activated co-reactant, optimizing the efficiency and responsiveness of ECL.

In our experiments, titania nanostructured films have been modified in order to obtain layered-structure 3D mesoporous electrodes, where the outer part of the film is functionalized with a luminophore. The thickness of such functionalized layer was varied from a few hundred nanometers from the outer surface down to the whole film thickness. This allows to control the ECL characteristics of the film and to get some insight into the mechanisms involved in the process.

Acknowledgements: financial support of MUR, PRIN 2017FJCPEX "3D-FARE", is gratefully acknowledged.

[1] Tingting Han et al. J. Electroanal. Chem. 902 (2021) 115821
[2] E. Daviddi et al. ChemElectroChem 4(7) (2017) 1719.

PO059

Reversible formation of defects in HKUST-1: a surface perspective

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Metal–organic frameworks (MOFs) are widely studied nanoporous materials obtained from the coordination of metal ions or clusters (nodes) to polydentate organic molecules (linkers). This interaction yields three-dimensional structures featuring pores with ultrahigh internal surface areas (up to 10 000 m2 g−1) and highly reactive metal sites, to be exploited in a vast plethora of applications [1]. HKUST-1, a MOF containing Cu(II) and BTC (benzene-1,3,5-tricarboxilate), has been extensively characterized both for the reactivity of its open copper sites and the reversible formation of structural, “engineered” defective sites exhibiting Cu(I)/Cu(II) dimers [2]. However, despite the significant scientific effort, a full consensus on the formation, structure, and reactivity of the defects is yet to be reached. Such an understanding is crucial for the efficient application of HKUST-1 both in catalysis and in the capture of CO_2, in which the defective sites play an important role. Here, we report new insights into the formation of Cu(I) defects on the surface of HKUST-1 gained with a newly developed setup for *operando* Ambient Pressure Near Edge X-ray Absorption Fine Structure (AP-NEXAFS) measurements [3]. Our proposed mechanism consists in a Cu(II)-catalyzed oxidative decarboxylation of the BTC ligand leading to Cu(I)/Cu(II) dimers where both copper atoms are coordinated by only three oxygen atoms [4]. Further, we prove that this process can be fully reversed by exposing the MOF to a CO_2 flux at ambient pressure, which also completely inhibits the H_2-induced reduction of the metal sites, and we quantify the surface ratio of the defective dimers formed (ca. 45%, much higher than the bulk ratio). We believe that our findings may lead to an increased understanding of the surface properties of HKUST-1 and pave the way for their rational use in catalytic and CO_2 uptake processes.

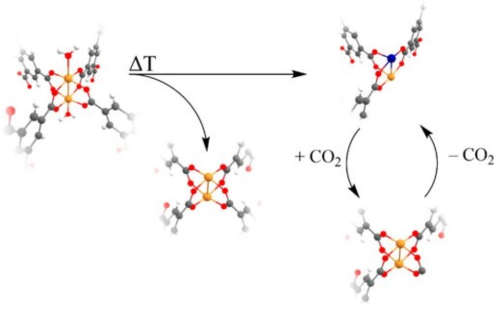

Figure 1 Proposed mechanism for the reversible formation of Cu(I)/Cu(II) defective sites in HKUST-1.

[1] H. Furukawa et al. Science 341 (6149) 1230444
[2] M. Todato et al. J. Phys. Chem. C 120 (2016) 12879-12889
[3] C. Castán-Guerrero et al. Rev. Sci. Instrum. 89 (2018) 05401
[4] L. Braglia et al. J. Phys. Chem. Lett. 12 (2021) 9182-9187

PO060

Phase separation behavior and structural role of amylose and amylopectin in PVA/starch hybrid networks: taking a step back to gain broader perspectives

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The constant increase in production, use, and disposal of synthetic plastic represents a concerning threat to the sustainability of our ecosystem. A possible strategy to reduce the consumption of synthetic polymers is to blend them with available natural products. A well-established couple for the production of biocomposite plastic materials is represented by Poly(Vinyl-Alcohol) (PVA) and starch. Nevertheless, the interactions between PVA and starch's polymeric components (amylose and amylopectin) are still a matter of debate. In this contribution, we prepared and analyzed simple PVA/amylose, PVA/amylopectin, and PVA/amylose/amylopectin systems in order to formulate a wider theoretical framework that describes said interactions and their consequences on the features of PVA/starch-based materials. Investigation of PVA/amylose, PVA/amylopectin, and PVA/amylose/amylopectin systems with variable PVA/polysaccharide ratios allowed a deeper understanding of the possible evolution of a real PVA/starch cryogel. Thanks to Confocal Laser Scanning Microscopy (CLSM) on pre-gel fluorescently labeled solutions, we determined the absence of miscibility between PVA and amylose, as well as PVA and amylopectin, in the considered temperature range (25-98°C). In PVA solutions, amylose shows a supramolecular arrangement, reasonably corresponding to single helixes forming liquid crystals with nematic order. Instead, PVA and amylopectin solutions show liquid-liquid phase separation.

In the cryogels, for PVA:polysaccharide ratios of 2:1, the heteropolymeric interactions are strongly unfavored, whereas PVA-PVA interactions are increased, leading to the formation of more compact and crystalline PVA networks. The maximum extent of PVA polysaccharide interactions is likely to occur at a 1:1 ratio. Nevertheless, PVA amylopectin interactions are "destructive", given the inability of amylopectin to form proper networks, while PVA-amylose interactions can be "constructive" and lead to the formation of hybrid tie points in the gel, containing both the polymers in strong association, as suggested by Differential Scanning Calorimetry (DSC) and Small Angle X-Ray Scattering (SAXS) measurements.

As an example of the implications that this broader knowledge could have, we provided a prevision of the variation of one simple parameter (the gel fraction) for any possible PVA/amylose/amylopectin mixing ratio and preliminarily tested its validity on a real PVA/starch sample.

PO061

Surface-functionalized TiO_2/PEO composite electrolytes for all-solid-state lithium metal batteries

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The use of mechanically strong nanocomposite solid state electrolytes (SSEs) has largely proved its effectiveness for the implementation of lithium metal batteries (LMBs), otherwise plagued by severe dendrite growth, thanks to the possibility of coupling the flexibility of polymeric matrixes with the improved toughness imparted by ceramic dispersoids [1]. In particular, the use of functionalized fillers has permitted to encompass elevate amounts (>20% wt%) of inorganic fillers without compromising the homogeneity and the performances of the SSE [2]. Due to this reason and considering that such ceramic fillers (SiO_2, TiO_2, …) usually present a non-negligible reactivity with respect to lithium, it results no more possible to disregard the possible chemical interactions established between them and the growing lithium dendrites [3].

Therefore, starting from a work already published by this group [4], a nanocomposite SSE based on TiO_2 NPs functionalized with short chains of PEO_{5K} and encompassed into high Mw PEO_{4M} is first tested for its stability against lithium dendrites demonstrating a certain degree of self-healing behavior, probably related to the interaction between lithium dendrites and hybrid fillers. Subsequently, this hypothetical interaction is carefully investigated using both in situ and ex situ analyses such as transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), mechanical testing, time-dependent nuclear magnetic resonance (TD-NMR), and electrochemical techniques. Overall, even if the possible electrochemical lithiation of such fillers is confirmed, only a strongly reduced interaction between Li and TiO_2 is observed during in-situ testing. Consequently, the incredible performances of these nanocomposite SSEs can be mainly attributed to the improved mechanical properties imparted by the high amount of ceramic material (18% wt) dispersed into the electrolyte and only marginally by a dendrite-eating behaviour instated by TiO_2 lithiation.

[1] D. Lin et al. Nature Nanotechnology 2017, 12 (3), 194-206
[2] L. Mezzomo et al. Electrochimica Acta 2022, 411, 140060
[3] K. Liu et al. Advanced Materials 2017, 29 (4), 1-6
[4] F. Colombo et al. Journal of the Electrochemical Society 2020, 167 (7), 070535

PO062

Biobased redox electrolytes for advanced supercapacitors

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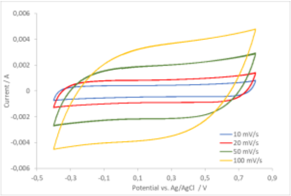
The electrification of our energy habits is the new paradigm for a sustainable society. Nonetheless, key enabling electrochemical energy storage technologies are still based on a linear approach to the use of raw materials, which are critical in terms of supply chain for environmental, economic, social, and geo-political factors. Among energy storage devices, supercapacitors present unique advantages for their intrinsic superior eco-friendliness and safety, long life, and high charge/discharge rates. The main limit of supercapacitors is their relatively low energy density due to the capacitive mechanism of charge storage. To improve energy densities and expand supercapacitors applications, several concepts mainly based on adding faradaic contributions to the capacitive storage have been proposed. [1] An interesting approach is the use of natural antioxidants as redox additives to the electrolyte or to the electrode material. [2] We demonstrated the proof-of-concept of a device with increased energy density based on the use of brewed coffee as biobased redox electrolyte.



The faradaic contributions increasing the energy density are attributed to the abundance of chlorogenic acids in coffee. Furthermore, the device was fabricated with a current collector based on a novel metal-free carbon-biopolymer composite derived from bio- based activated carbons together with a biobased binder, to preserve both bio-derivation and potential bio-degradability.

The preliminary findings demonstrate the feasibility of using complex natural extracts of polyphenols as redox active electrolytes for advanced storage devices, thus proposing a new field of exploitation for (waste) agri-food biomasses: a single natural source can provide both lignocellulosic raw material for nanostructured carbons for capacitive storage, [3] and antioxidants as redox active molecules, combined for hybrid supercapacitors with improved energy density.

Acknowledgment

The Project IEMAP - Materiali Avanzati per l'Energia, MISE-Mission Innovation Program 2021-202 is grateful acknowledged.

[1] K. Nasrin et al. Energy Fuels 2021, 35, 6465−6482
[2] T. Wang et al. J. Mater. Chem. A, 2021, 9, 11839
[3] P. Stufano et al. MRS Energy and Sustainability,2022 under review

PO063

Laser ablation in solution for a more sustainable perovskite-based solar cells

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In the last decade, lead halide perovskite (LHP) materials have drawn enormous attention and found application in a variety of optoelectronic devices, like light-emitting diodes, solar cells, transistors, gas sensors, and photodetectors.[1] Such a high versatility is attributable to their long carrier diffusion lengths, simple bandgap tunability, high absorption coefficients, and exceptional defect tolerance [2] which makes solution-processing in ambient condition a viable prospect.[3] These properties, together with the relatively low cost of perovskite precursor salts, made perovskite-based optoelectronics gaining substantial commercial appeal in the last years. The main challenges for their commercialization, are stability, scalability, and sustainability. For an effective scale-up the toxic solvents commonly used for LHPs synthesis and/or thin-films deposition must be replaced with eco-friendly ones.[4] Recently, laser ablation in solution (LASiS) was proposed as an alternative top-down approach to synthesize LHP nanocrystals (NCs) in ambient conditions.[5] The relevant features of the nanocrystals synthesis are: (i) the presence of a graphitic/graphene phase linked to the perovskite ones, which improve their stability in ambient conditions and under electric field [6] and (ii) the possibility to completely avoid toxic solvents to obtain good-emissive LHP nanocrystals using eco-friendly alcohols. [7] By combining this methodology with a scalable deposition technique, such as spray-coating, both scalability and sustainability of perovskite-based solar cells can be improved. Spray-coating was also shown to be important for depositing perovskite thin-films onto non-flat substrates, which found application in textured silicon-perovskite tandem solar cells.[8]

[1] Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; et al. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* 2021, 15 (7), 10775–10981;

[2] Manser, J. S.; Christians, J. A.; Kamat, P. V. Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev*. 2016, 116 (21), 12956–13008;

[3] Du, Y.; Liu, P.; Li, F.; Hou, X.; Zhang, H.; Shi, Y.; Wang, S.; Wang, Y.; Guo, S.; Tai, Q.; et al. Precursor Engineering for Performance Enhancement of Hole-Transport-Layer-Free Carbon-Based MAPbBr3 Perovskite Solar Cells. *J. Alloys Compd*. 2020, 154902;

[4] Brown, A. A. M.; Damodaran, B.; Jiang, L.; Tey, J. N.; Pu, S. H.; Mathews, N.; Mhaisalkar, S. G. Lead Halide Perovskite Nanocrystals: Room Temperature Syntheses toward Commercial Viability. *Adv. Energy Mater*. 2020, 2001349, 1–19;

[5] F. Lamberti, L. Litti, M. De Bastiani, R. Sorrentino, M. Meneghetti, A. Petrozza - *Adv. Energy Mater*. 2017, 7, 1601703;

[6] A. Rizzo, F. Lamberti, M. Buonomo, N. Wrachien, L. Torto, N. Lago, S. Sansoni, R. Pilot, M. Prato, N. Michieli, M. Meneghetti, G. Meneghesso, A. Cester - *Sol. Energy Mater. Sol. Cells* 2019, 189, 43-52;

[7] S. Sansoni, F. M. Anoè, M. Meneghetti - Synthesis of CsPbBr3Nanocrystals via LaserAblation in Alcohol for More Sustainable Perovskite-based Optoelectronics (Under Submission);

[8] S. Sansoni, M. De Bastiani, E. Aydin, E. Ugur, F. H. Isikgor, A. Zahrani, F. Lamberti, F. Laquai, M. Meneghetti, and S. De Wolf - *Adv. Mater. Technol.* 2020, 5, 1901009.

PO064

A Simple Root to Synthesize Carbon Dots with High Photobleaching Resistance and Efficient On-Off Switchable Fluorescence

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Carbon Dots (CDs) are nanometre sized carbon particles characterized by very interesting photoluminescence (PL) properties in the visible light range. Their intrinsic eco-friendly structure, entirely based on carbon, combined with their attractive PL, makes these nanoparticles very attractive for a variety of application areas [1]. Therefore, recently, many studies have aimed at developing various synthetic routes for CDs displaying different PL properties across the whole visible range. Broadly speaking, such synthetic approaches involve thermal carbonization of opportunely selected organic molecules via different heating methods [2].

In this work, CDs are synthesized trough a glycothermal treatment of resorcinol (1,3-hydroxybenzene) in an open reactor [3]. The adoption of such synthetic strategy is motivated by the possibility of (i) efficiently removing water (forming as secondary product) by evaporation and (ii) to monitor the evolution of fluorescence during the synthesis.

The as-obtained CDs display two fluorescence bands, in the green and in the blue. The former is ascribed to polycyclic aromatic hydrocarbons (PAHs) within CDs, originated by resorcinol polycondensations, the latter to CDs surface states emission. The rate of the reaction could be increased by introducing catalysts (namely NaOH and H_2SO_4) in the reaction solution. By studying variations of the CDs PL under prolonged exposure to UV irradiation, we can show that PAHs green fluorescence has a high photobleaching resistance. Finally, the green emission of CDs demonstrates a marked quenching/enhancing effect in the presence of acidic or basic compounds, which suggests a profitable use of such CDs in pH-responsive devices or on/off sensors.

[1] Y. Wang et al. J. Mater. Chem. C 2 (2014) 6921–39
[2] A. Sciortino et al. C 4 (2018) 67
A. Panniello et al. J. Phys. Chem. C 122 (2018) 839–49
G. Minervini et al. Materials 13 (2020) 3716
[3] Minervini et al. Submitted (2022)
F. Yuan et al. Nature Communications 9 (2018) 2249
F. Yuan Nano Research 12 (2019) 1669-1674
T. Yoshinaga ACS Omega 6 (2021) 1741–50F

PO065

Can Domain-Based Local Pair Natural Orbitals Approaches Accurately Predict Phosphorescence Energies?

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Since the discovery of the peculiar conducting and optical properties of aromatics, many efforts have been made to describe their phosphorescence. However, the complex electronic structure of their spin states requires correlated wavefunction-based methods, which are only applicable to small model systems in the canonical implementation [1–3]. The linear scaling DLPNO-CCSD(T) method [4–7] which reproduces typically 99.8-99.9% of the canonical correlation energy [8], was employed for the calculation of singlet-triplet gap of aromatics. Both accuracy and efficiency of our protocol in relation to the main parameters of the calculation (basis set, triples correction approximation, dimension of Pair Natural Orbitals space) were investigated. Two settings were proposed, showing an excellent agreement with experimental data: (i) the very accurate "Gold DLPNO-CCSD(T)" for systems of medium size; (ii) the cost-effective "Silver DLPNO-CCSD(T)" for very large chemicals. Besides, the Silver DLPNO-CCSD(T) method was used to compute the phosphorescence gap, spectra and rate constants of prototype carbazolyl dicyanobenzene (CDCB) compounds in toluene. A very good agreement was found between theory and experiment, which suggests that our computational protocol is potentially broadly applicable, opening new avenues for the calculation of the photophysical properties of aromatic compounds.

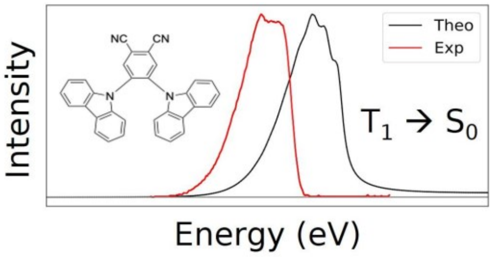

Figure 1: Computed phosphorescence spectrum of 4,5-Bis(carbazol-9-yl)-1,2-dicyanobenzene (2CzPN) by employing Silver DLPNO-CCSD(T) well-to-well singlet-triplet gap (black curve) and corresponding experimental spectrum [9] (red curve).

[1] Krylov, A. I. In Reviews in Computational Chemistry; John Wiley Sons, Ltd: 2017; Chapter 4, pp 151–224.
[2] Zimmerman, P. M. The Journal of Physical Chemistry A 2017, 121, PMID: 28530830, 4712–4720.
[3] Hajgat´o, B.; Szieberth, D.; Geerlings, P.; De Proft, F.; Deleuze, M. S. The Journal of Chemical Physics 2009, 131, 224321.
[4] Meyer, W. International Journal of Quantum Chemistry 1971, 5, 341–348.
[5] Neese, F.; Wennmohs, F.; Hansen, A. The Journal of Chemical Physics 2009, 130, 114108.
[6] Riplinger, C.; Neese, F. The Journal of Chemical Physics 2013, 138, 034106.
[7] Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. The Journal of Chemical Physics 2013, 139, 134101.
[8] Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. The Journal of Chemical Physics 2016, 144, 024109
[9] Hosokai, T.; Matsuzaki, H.; Nakanotani, H.; Tokumaru, K.; Tsutsui, T.; Furube, A; Nasu, K.; Nomura, H.; Yahiro, M. and Adachi, C. Science Advances, vol.3, no.5, 2017.

PO113

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AmSpec presents *AmSpec Academy*: leading company in inspections & testing services meets university

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AmSpec Academy is a project held by University of Genoa and AmSpec Italia, born to bring together two worlds, university and work, by introducing students to the company and carrying out a research project.

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AmSpec Academy's research is aiming at ecological transition, beginning from the production of HVO (hydrotreated vegetable oil), an alternative and promising fuel obtained from the treatment of waste biomasses[1].
The project involves using a pilot reactor to fine-tune a catalytic hydrotreatment in laboratory scale of biomasses to obtain an hydrocarburic mixture that will reproduce current fuels' behaviour in engines.
Such mixture produced will be tested according to European test methods to evaluate stability, performance and process sustainability.

[1] Mikkonen, Seppo, Honkanen, Markku, and Kuronen, Markku. HVO, hydrotreated vegetable oil. A premium renewable biofuel for diesel engines. Germany: N. p., 2013. Web.

PS001

Experimental study of airborne transmission of viruses in AMT Genoa public transport system

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In the present work a 18 meter long public bus (Mercedes Citaro G) of the AMT Spa fleet has been modeled using a computational approach developed by the University of Genova in order to simulate the evolution of the COVID infection from an infected passenger. The computational model has been validated with an experimental campaign on the same bus during several hours of operation in Genova city. A specific experimental protocol has been developed by the researchers of the University to reproduce the emissions from an infected passenger and to detect, measure, the infected area into the bus. A mannequin equipped with a water spray emitter is used to reproduce the infectious passenger and the infected area is quantified using series of probes made of cotton filters distributed and stuck in different areas of the bus. The amount of emission on each probe is measured to identify the infected area. The internal geometry of the bus has been reconstructed with high fidelity using photogrammetry techniques from an existing vehicle. The main details needed for the modeling of the real flow structure have been taken into consideration, including passenger handles, barriers near the door, the windows as vasistas. The bus is equipped with a ventilation system for air conditioning, guaranteed through diffusers for the air inlet, placed on the roof laterally and for the entire length of the vehicle (both on the right and on the left); on the roof there are two grids for the intake of exhausted air (one for each compartment). The air conditioning system on the bus has been modeled with air exchange frequency ACH=100 (corresponding to the 57% of the maximum air exchange of the Mercedes Citaro-G). The internal flow recirculation has been taken into account with a filtering efficiency equal to 50%; the recirculated filtered flow is re-injected into the air conditioning delivery. Several situations have been considered by varying the infected passenger position (front, mid, rear bus seats) and the travel duration (15-30 minutes). A post-processing method for the numerical results has been developed to identify the infection content at every position into the bus and to quantify the probability of infection according to models from open literature. The effects of the protecting mask have been modelled and different scenarios has been considered: no one inside the bus wears the mask, everybody but the infected wears the mask, everyone (including the infected passenger) wears the mask. The distributions of the risk inside the bus have been quantified and compared to the corresponding experimental data: a very good match has been obtained. It has been concluded that if everybody has the mask the probability of infection inside the bus is not higher than in most common situations of everyday life (supermarket, church, patrol station, …)

PS002

IREOS S.p.A. - plastics recovery from the marine environment

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For over 40 years, IREOS S.p.A. offers environmental services supported by over 120 collaborators, trained and professional staff, as well as the collaboration of the most qualified experts in the sector. IREOS performs, with its own structures, characterizations and analytical investigations on sites, land and aquifer remediation in industrial and civil areas, remediation of asbestos and other dangerous substances on industrial and civil plants and buildings, coordinates and organizes, even on plants directly or indirectly connected to the same, waste recovery and/or disposal services, builds and manages plants connected to the waste cycle, being able to solve problems of a chemical nature and treatment of hazardous and non-hazardous waste. A structured internal Research & Development department and a specific partnership agreement with the University of Genoa (DCCI), in force since 2015, a ten-year collaboration with the IPCB-CNR of Naples and with University of Naples (Federico II University), guarantee the basis for the development of multiple activities related to the environmental sector with a specific objective linked to the recovery of material, whether of industrial origin - in particular plastics - or of natural origin - soils, clays, rocks -, to the saving of natural resources and to the reduction of emissions into the atmosphere. The last successfully completed project involved the study of plastics present in the sea, their recovery and reuse. The project called SiRIMaP "Innovative Detection Systems for the monitoring of Marine Pollution from Plastics and subsequent recovery and recycling", facilitated under the PON 2014-20 program, was developed with the following proposing partners: the DAC (Campania Aerospace Technological District) Lead partner, UNIBS (University of Brescia) and UNIMOL (University of Molise), in addition to the collaboration of UNIPARTHENOPE, MAPSAT, CALTEC / OMI, CNR ISASI, CNR IAS, CNR ICAR, CNR IPCB. The project has created a new localization system at sea of macro, meso and microplastics through the use of remote and proximity platforms, systems for sampling, methodologies for their analysis in situ and in the laboratory and in the development appropriate recovery and recycling strategies. The results obtained by SiRIMaP appear particularly relevant for the protection of the Mediterranean Sea, recently identified as a region of accumulation of plastic debris. In this scenario, SiRIMaP represents a strategic proposal for the "Blue Growth" area of specialization, and in line with the development guidelines defined at world, European and national level. The results obtained have allowed the conception, design and construction of demonstrators with a high degree of innovation, including the lines of treatment and recovery of plastics by IREOS.

PS003

What do we expect from Physical Chemistry research? Nothing else than saving the world

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PS004

Using SRF as an energy alternative

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SRF, Solid Recovered Fuel, is a fuel obtained from the dry component (plastics, paper, textile fibers, etc.) of non-hazardous waste, both municipal and special, through special separation treatments from other non-combustible materials.

Plants that use SRF as a fuel, can be dedicated or existing plants that also use traditional fuels, in both cases the plants are characterized by combustion and flue gas cleaning technologies capable of meeting regulatory limits.

In Italy, SRF can be used as a fuel, only if it is recognized as CSS-combustibile, in cement plants with a production capacity of more than 500 tons/d of clinker and in thermoelectric power plants with a thermal combustion capacity of more than 50 MW.

ReLife firmly believes in the importance of this fuel, since it has a di double advantage: emissions are much lower than other fuels and the amount of waste destined for disposal in landfills is decreased.

In ReFuel, thanks to a state-of-the-art, highly automated plant (as many as 4 optical readers to remove chlorine-based fractions), Secondary Solid Fuel is destined as a substitute for coal in cement factories and power plants.

Referring to the requirements prescribed by EN ISO 21640:2021 "Specifications and classes" for the classification of secondary solid fuels, in our ReFuel plant we are able to produce a very high quality SRF with a lower heating value of class 2 and a chlorine and mercury content that falls within class 1.

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