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E TECNOLOGIA DEI MATERIALI (INSTM)

XIV CONVEGNO NAZIONALE SULLA SCIENZA E TECNOLOGIA DEI MATERIALI

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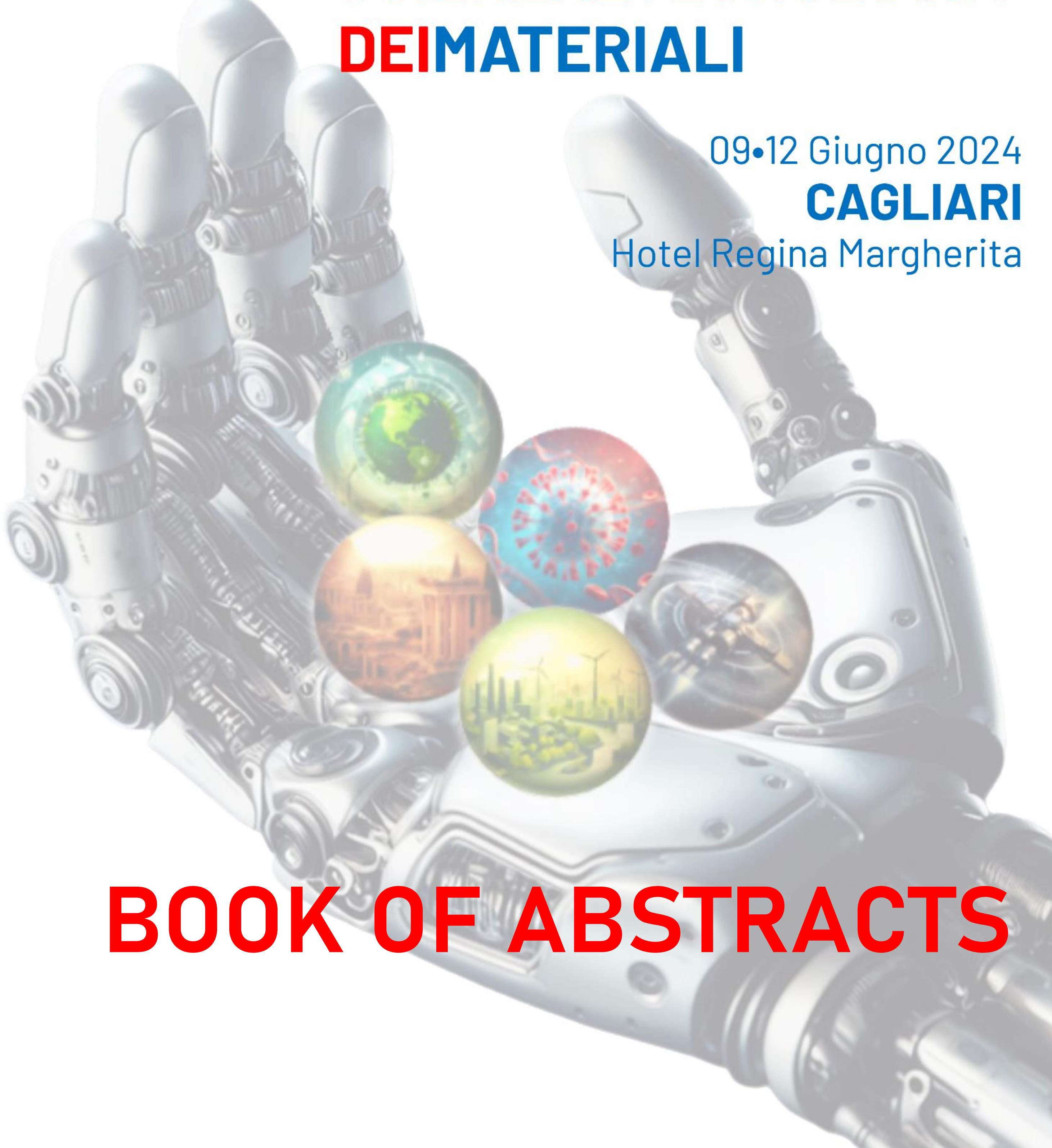

BOOK OF ABSTRACTS

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vi diamo un caloroso benvenuto al XIV Convegno INSTM sulla Scienza e Tecnologia dei Materiali. Il Convegno rappresenta, tradizionalmente, un momento di incontro tra coloro che operano, a vario titolo, nel settore della Scienza e Tecnologia dei Materiali e offrirà uno spazio propedeutico al dialogo e creare nuove opportunità di interazione e collaborazione per la vasta comunità scientifica INSTM.

Il Convegno riporterà le attività svolte dagli afferenti INSTM e offrirà spunti di riflessione e confronto sulle nuove sfide della ricerca all'interno del Consorzio. Sarà l'occasione per discutere aspetti fondamentali, innovativi e applicativi sulla scienza e tecnologia dei materiali e per promuovere una piena integrazione e un confronto interdisciplinare tra i partecipanti. Pertanto, il programma scientifico offrirà approfondimenti più specifici e sezioni più generali interdisciplinari, e fornirà spazio e visibilità ai giovani ricercatori, stimolando al contempo l'organizzazione di progetti di ricerca comuni.

Il programma scientifico si articolerà in cinque sessioni tematiche:

- Materiali e tecnologie per il manifatturiero avanzato, il Made in Italy e l'aerospazio
- Materiali e tecnologie per l'energia per la transizione ecologica e la mobilità sostenibile
- Materiali e tecnologie per l'economia verde e l'economia circolare
- Materiali e tecnologie per il costruito e il patrimonio culturale
- Materiali e tecnologie per le scienze della vita e le scienze dell'alimentazione

Il programma scientifico prevede, 5 Key Notes, 124 interventi orali (69 Oral e 55 Short Oral), 114 poster, e una comunicazione trasversale. Complessivamente, il Convegno offrirà interventi di Università, Centri di Ricerca e Industrie. Questo denso e stimolante programma è condensato in questo Libro Atti, che è disponibile in forma elettronica per tutti i partecipanti e sponsor.

I nostri ringraziamenti vanno ai membri del Comitato Organizzatore e del Comitato Scientifico e a tutto lo staff INSTM di Firenze. Ringraziamo gli Sponsor e gli Enti patrocinanti per il loro fondamentale contributo e la loro attenzione alla Ricerca e Innovazione.

Ci auguriamo davvero che questa conferenza vi piaccia almeno quanto noi ci siamo divertiti a organizzarla.

Cagliari, 9 giugno 2024

Le Chair

Prof.ssa Cecilia Bartuli
Prof.ssa Lucia Curri

INDEX

KEY
NOTES

NOVEL MATERIALS CHEMISTRY FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

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The current trend in various energy applications, ranging from batteries to electrolizers, lays in the control of structural, physicochemical and morphological properties of materials and their interfaces. During this presentation, recent scalable strategies for nanostructured materials synthesis, targeting energy and environmental applications will be discussed. Especially, we will focus on one-pot strategies for the fabrication of hybrid and complex nanomaterials focusing on the importance of the organic-inorganic and inorganic-inorganic interfaces. Among the examples presented, we will discuss the synthesis of complex nanostructures and the stabilization of metastable phases for applications in energy storage and conversion. We will see that nowadays the available strategies allow a control in terms of composition, crystalline structure, morphology and nanostructuration that would have been unimaginable just few years ago. Finally, the open challenges the field is currently facing and possible further developments which are needed to meet the always growing demand for high performing materials will be also discussed.

FROM WASTE TO PRODUCT: EXAMPLES OF CIRCULARITY

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Solid waste generated by the municipal and industrial sectors is a major problem worldwide due to issues of collection, transportation, treatment, and disposal. The recycling and re-use of solid waste represent a great opportunity in terms of resource-saving, environmental protection, and economic development. A way to valorise waste is thermochemical transformation via pyrolysis. In this context, the biochar obtained from wastes has shown promising characteristics for its application as a soil conditioner, anode for Li-ion batteries (LIBs), support for catalysts, cosmetics, and finally as a biocharm. In the current study, the applications of biochar from different wastes in LIBs, and cosmetics will be investigated.

Waste feedstocks: Artichoke, hazelnut shells, broken rice grains, rice husks, vine wood waste, barley waste, Sargassum, and leather shaving waste.

Activated biochar (ACB) synthesis: pyrolysis under N_2 flow of 100 mL/min, at 700 °C, 30 min and physical activation using steam at 850 °C for 180 minutes, heating rate 10 °C/min, $H_2O:N_2=1:1$ flow (100 mL/min), or by CO_2 of 100 mL/min for 240 minutes.

Cosmetics: Inulin, polyphenols, etc. were extracted from artichoke for designing hair cosmetics. The fibrous waste was applied to the pyrolysis process and the obtained ACB was used in the face mask's formulation.

LIBs: ACB from leather waste was designed as an anode for the half-cell and full-cell LIBs application.

In cosmetics, artichoke extracts were highly efficient in the formulation of cosmetics for hair polishing and protective pre-drying treatment, pre-shampoo for skin and roots, and after-wash masks. The ACB obtained from fibrous waste was very fruitful in face purification masks.

In LIBs, a good rate capability and cycling performance were obtained in the half-cell test in addition to an initial discharge capacity of about 160 mA h g^{-1} with acceptable cycling stability at 0.1 C in full-cell using ACB from tannery waste as the anode.

In cosmetics, the high surface area and porous texture of ABS helped with the high absorbency efficiency of face purification masks. In LIBs, the promising performance of ACB from tannery waste was associated with the synergistic effect of interlayer spacing, defects, N, O, and S-doped, high specific surface area, and micro-mesopore texture. Overall, selecting the proper biomass waste and optimizing the best pyrolysis and activation conditions could help in achieving the best ABS properties for each application.

TOWARDS THE DEVELOPMENT OF GREEN STRATEGIES FOR THE CONSERVATION OF CULTURAL HERITAGE: THE GOGREEN AND SUPERSTAR PROJECTS

Prati S[1]

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In the age of the ecological transition, there is an increasing demand related to the development of new green methods for the conservation and restoration of cultural heritage. In particular, a great attention is devoted to the development of materials and methods which not only can safeguard the integrity of the work of art, but also are safe both for the operator and the environment.

In this context, my research group has so far developed different formulations obtained with biopolymers such as polyhydroxybutirate and agar in combination with green solvents of different polarity (Dimethylcarbonate, γ-Valerolactone, Ethyl Lactate, Biodiesel, green Deep Euctetic Solvents) for the selective removal of different types of unwanted layers from several types of artistic artefacts such as movable and immovable paintings, metal objects, paper substrates, cinematographic movies.

In the frame of the European Project GOGREEN and the National Italian Project Superstar electrospun (ES) materials are being developed as carrier of green gels and solvents.

The micro-nano porosity of the nonwoven material is effective in the removal of varnishes applied on paintings exploiting a peel off effect which avoids any further mechanical action. First tests were performed using nylon 6,6 which has been now substituted by a greener alternative based on pullulan. The pullulan based non wovens have been also functionalized with a photoactive material capable of producing a localized increase of temperature when enlighted with a visible source. In this way high insoluble coatings such as alkyd resin employed in spray can be selectively removed. First tests on street art have been performed.

To evaluate the performance of the new methods ad hoc analytical methods are actually under optimisation to evaluate the cleaning efficacy and the effects on the above painting layer.

Sustainable Preservation Strategies for Street Art (SuPerStAr) funded by MUR, PRIN; Green Strategies To Conserve The Past And Preserve The Future Of Cultural Heritage (GOGREEN); financing institution: EUROPEAN COMMISSION (HORIZON EUROPE).

A special thanks to all the co-authors of the papers already published and under publication on this topic.

INNOVATION AT THE HEART OF OUR STRATEGY: HOW ESSILORLUXOTTICA IS EXPANDING THE BOUNDARIES OF EYEWEAR AND VISION CARE

Ferracane F[1,2,3]

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EssilorLuxottica is a European vertically integrated globally operating Company. We trust in the open network approach, and we are strongly Mission-driven. As a leading company in world-class vision care products, EssilorLuxottica is developing innovation in world-class vision care products, combining lenses and frames under the same roof at the intersection of med-tech, digital, luxury and now hearing solutions. The company powerful Mission consist in helping the world to 'see more and be more'. How can we do it? EssilorLuxottica has a unique approach based on the vertical integrated business model. Overseeing the entire process from design to distribution guarantees the highest level of quality and gives the company a unique understanding of customer trends and testes. This business model is possible thanks to a strong strategic acquisition approach, that is the heart of EssilorLuxottica's growth. In EssilorLuxottica there is a strong culture of innovation, driven by a strong product differentiation and fast go to market approach. The product innovation workflow is based on a waterfall approach, through ideation, feasibility, and proof of concept phases. Focusing on Sun Lenses, R&D is driven by five routs: Lens to last, Sustainability, Vision experience, boost aesthetic design and Tech enhancing. Then, in the end, a focus on a real case study will be presented: "Ray-ban Reverse, The Very First of Its Kind".

FROM MICRO-ENGINEERED BIOMATERIALS TO MINI-BONES

Tahmasebi Birgani ZN[1]

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Miniaturized in vitro bone models or tissues, referred to as "mini-bones", are submillimeter tissues designed to replicate the intricate nature of bone. These models have been developed in various forms, including cell-laden hydrogels or microscaffolds, organ-on-chips, and self-assembled cellular aggregates. Mini-bones are emerging as valuable tools in bone-related research, for example, for studying the pathophysiology and regenerative mechanisms of bone, and developing new medications and regenerative therapies. Bone tissue comprises a dynamic, hierarchically organized extracellular matrix (ECM) with unique mechanical properties and vital biochemical functions, within which various types of specialized cells are distributed. Replicating this complex, hierarchical organization is essential to capture the mechanical and biochemical functions of bone. To achieve this, my team employs a bottom-up tissue engineering approach, which relies on guided or random assembly of cell and biomaterial building blocks, to construct three-dimensional modular tissues that recapitulate the nano-/micro- to meso/macro-structural organization of their native counterparts. Bottom-up engineered tissues are often made from cells alone, and typically exhibit limited mechanical stiffness and lack the proper ECM required for engineering bone. To address this limitation, our research focuses on fabricating bottom-up engineered mini-bones that contain bone-mimetic, in situ-formed micromatrices, or cell-assemblable microparticles made from biomaterials that are similar to bone ECM. We utilize various microfabrication technologies to generate these biomaterials and enrich them with cell- and tissue-instructive chemical, physical, and biological information. These microengineered biomaterials modulate cellular assembly or tissue remodeling, deliver cell-instructive, bioactive cues, and ultimately, mimic the ECM functions in mini-bones.

TRASVERSAL
ORAL

A REPEATABILITY AND REPRODUCIBILITY STUDY OF A 3D PRINTED MICRO-OPTOFLUIDIC DEVICE FOR TWO-PHASE FLOW MONITORING AND CONTROL

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Microfluidic devices have emerged as promising tools for lab-on-chip applications across biomedical, biological, and chemical fields. Nowadys, the most widespread fabrication method for microfluidic devices is soft-lithography based on PDMS (polydimethylsiloxane), which still faces several repeatability and reproducibility challenges. In this work, to address this challenge, micro-optofluidic (MoF) devices, featuring a microchannel of 400×400μm2, for two-phase flow control and monitoring were 3D printed via Projection Microstereolithography. In fact, the advent of 3D printing to the microfluidic field has revolutionized the fabrication process, since allows for high-resolution and sub-micron precision, enabling the fabrication of monolithic parts with low variability. The devices were fabricated and tested by exploiting an optical detection approach. Two different two-phase flow processes were investigated: an air-water bi-phase flow and a two-phase mixture composed of cells suspended on PBS. The results' repeatability and reproducibility were rationalized by mean of a Design of Experiment (DoE) approach.

The MoF devices were fabricated using two photo-curable resins: HTL and BIO (BMF, Maynard, MA, USA). The former was used for the analysis of air-water bi-phase flow. While the latter for the MoF device used as cell (eukaryotic yeast cells of *Saccharomyces cerevisiae*) concentration detector, since is a biocompatible grade. The devices were fabricated on a microArch®S140 3D printer (BMF, Maynard, MA, USA).

For both air-water (process 1) and cells-PBS (process 2) bi-phase flows we have identified the optimized operating conditions, i.e., the optimal values for the flow rate (FR) and input laser power (P) to monitor the processes with a high repeatability and reproducibility. For the process 1, the configuration (P,FR)=(5 mW;0.3 mL/min) allowed to perform a better discrimination of the two investigated fluids and good hydrodynamic flow stability within the microchannel. While, regarding the process 2, with a FR=0.1 mL/min and $P \in \{1,3\}$ mW, we were able to discriminate between biological fluids with different concentrations of suspended cells with a robust working ability ($R^2 = 0.9874$; $R^2_{adj} = 0.9811$).

In this study, we investigated the performance of 3D printed MoF devices designed for monitoring and controlling two-phase flow processes. Our focus was on assessing the within-device repeatability and between-device reproducibility using a DoE approach. This goal was achieved by systematically varying the flow rate of the fluids and adjusting the laser input power across various levels to analyze their impact on hydrodynamic stability and optical detection performance, respectively.

ORAL

MAGNETIC MOLECULES FOR QUANTUM INFORMATION: THE CHALLENGE OF SINGLE SPIN ADDRESSING

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Implementation of advanced Quantum Technologies might benefit from the remarkable quantum properties and the chemical versatility shown by molecular spin systems based on the coordination bond. Molecules can also be processed to be deposited on surfaces, allowing the realization of hybrid nanostructures. However, the molecular approach also poses critical challenges. Achieving the control of a single molecule is one of the roadblocks to be removed. Using the electric field, which can be confined at the molecular scale, to control the spin degrees of freedom of the molecule is a possible route, but alternative approaches need to be explored. Learning from nature, we are proposing to exploit chirality as an alternative way to control the spin of molecular systems. The phenomenon of interest is known as chirality-induced spin selectivity or CISS. This effect pertains to the capability of chiral molecules to act as spin filters, i.e. selectively sorting flowing electrons based on their spin states. Most experimental pieces of evidence relied on transport measurements through molecules grafted on metallic surfaces, but recent results have shown that the effect can also be detected in electron transfer at the molecular levels thanks to the use of magnetic resonance spectroscopy. An overview of recent results and a perspective for an innovative spin-to-charge conversion for efficient spin readout will be presented.

DESIGN, SYNTHESIS, AND PROCESSING OF EXCHANGE-COUPLED NANOCOMPOSITES FOR ADVANCED PERMANENT MAGNETS

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Permanent magnets (PM) play a pivotal role in energy-related applications, and the quest for sustainable materials has refocused attention on ferrites, with $SrFe_{12}O_{19}$ (SFO) standing out. This study explores synthetic strategies, including cation substitution and exchange-coupling of magnetic phases, to enhance ferrite magnetic properties. Employing a scalable bottom-up sol-gel self-combustion process, we designed exchange-coupled nanocomposites ($SrFe_{12-x}Al_xO_{19}/CoFe_{2-y}Al_yO_4$ 90/10 wt%).

Monte Carlo simulations unveiled insights into the magnetic behavior, aligning with experimental findings. Structural analysis, including synchrotron X-ray powder diffraction and electron microscopy, highlighted controlled size, morphology, and composition of the nanocomposites. This integrated approach showcased the success of the sol-gel process in tailoring properties.

Spark plasma sintering (SPS) was employed to fabricate highly dense bulk magnets (SPS_NC and SPS_NC_SM). The SPS process, known for its efficiency [3], demonstrated the preservation of desired properties and improved alignment. Hysteresis loops, studied for randomly and parallel-oriented anisotropy axes, unraveled the intricate interplay of factors influencing magnetic properties. Importantly, the interface differences in NC and NC_SM nanocomposites were explored, shedding light on their unique characteristics.

Calculations of $(BH)_{max}$, representing the energy product, were conducted, further emphasizing the tailored magnetic properties achieved in this study. The exploration of interface variations, alongside the calculated (BH)max values, provides comprehensive insights into the design, synthesis, and processing of advanced permanent magnets, offering potential for sustainable energy applications.

PHOTOPHYSICAL PROPERTIES OF NEAR-INFRARED EMITTING LANTHANIDE-BASED HALIDE DOUBLE PEROVSKITES

Quochi F[1,2], Marongiu D[1], Liu F[1], Lai S[1], He Y[3], Slade TJ[3], Manna F[2,4], Mercuri ML[2,4], Kanatzidis MG[3], Saba M[1], Mura A[1], Bongiovanni G[1]

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Halide double perovskites are gaining increasing attention for various optoelectronic applications, such as photovoltaics, light-emitting diodes, and sensors, due to their unique properties. They offer advantages over traditional lead-based perovskites, including enhanced stability and reduced toxicity. Lanthanides, with their distinct electronic configurations, enhance functionality by introducing luminescence, magnetism, and stability. This study focuses on synthesizing and characterizing ytterbium- and erbium-based halide double perovskites for near-infrared (NIR) optical amplifiers and lasers, contributing to advancements in solid-state photonics.

Polycrystalline powders of double perovskites $Cs_2Na_xAg_{1-x}Ln_yBi_zIn_{1-y-z}Cl_6$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$) were synthesized by solvent evaporation of acidic solutions containing precursor salts. Comprehensive characterization of the materials was conducted using techniques such as powder X-ray Diffraction (pXRD), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), optical absorption spectroscopy, Raman spectroscopy, photoluminescence excitation (PLE) spectroscopy, photoluminescence quantum yield (PLQY) spectroscopy, and time-resolved photoluminescence (PL) spectroscopy with sub-nanosecond resolution. Additionally, single crystals of $Cs_2NaYbCl_6$ were grown using a vertical Bridgman furnace and characterized both structurally and spectroscopically.

pXRD analysis confirmed a single cubic phase in all samples, while precise control over materials composition was demonstrated via ICP-OES analysis. Materials rich in indium exhibited PLQYs reaching 90% for warm-white emission from self-trapped excitons and 10% for lanthanide emission. Using NIR-PL lifetime measurements and resonant absorption spectroscopy, we determined the lanthanide photophysical parameters, including radiative lifetimes and absorption/emission cross-section spectra, within the halide octahedral crystal field. Modeling optical gain enabled estimation of the figure-of-merit (FOM) of lanthanide-based double perovskites as NIR optical gain media. Structural and spectroscopic data on Cs2NaYbCl6 powder were confirmed in $Cs_2NaYbCl_6$ single crystals.

In summary, halide double perovskites demonstrated minimal lanthanide luminescence concentration quenching for Er and Yb concentrations up to 100 at. % ($y \approx 1$), attributed to the significant interionic distances within the double perovskite matrix. Evidence suggested a reduction in phonon-assisted relaxation within low-lying Er(III) electronic multiplets in Er-based double perovskites. Additionally, Er-based lasing at 1570 nm under 1530 nm optical pumping demonstrated an excellent FOM, distinguishing the halide double perovskite (HDP) crystal matrix from conventional crystal matrices such as yttrium aluminum garnet (YAG). Successful growth of high-purity single crystals is essential for advancing lanthanide-based halide double perovskites in the development of a new class of NIR solid-state lasers.

ENVIRONMENTALLY FRIENDLY PATHWAY TO KESTERITE NANOPARTICLES WITH CONTROLLABLE TIN CONTENT: AN IN-DEPTH STUDY OF MAGNETICAL AND OPTICAL PROPERTIES

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Over the last few decades, significant advancements have been made in the performance of thin-film chalcogenide solar cells. However, their reliance on expensive, toxic, and scanty elements poses environmental and economic challenges. In this context, Cu_2ZnSnS_4 (CZTS) emerges as a highly promising inorganic semiconducting compound for the production of low-cost thin-film photovoltaic devices since it is composed of easily available, cheap, non-poisonous and earth-abundant elements.

Here, we propose an environmentally friendly low-temperature synthetic pathway to produce Cu_2ZnSnS_4 nanoparticles with tuneable tin content. We investigated the shape, chemical composition, and phase with a multi-technique approach which includes High-Resolution Transmission Electron Microscopy, X-ray Photoelectron Spectroscopy, Energy Dispersive X-ray Spectroscopy, Inductively Coupled Plasma, and Micro-Raman spectroscopy. Additionally, the magnetic and magneto-optical properties have been explored by combining Electron Paramagnetic Resonance spectroscopy, SQUID magnetometry, and Magnetic Circular Dichroism to understand better the nature of defects present in the produced systems.

We developed a low-temperature synthetic path to produce kesterite Cu2ZnSnS4 nanoparticles with different tin content, resulting in the formation of quasi-spherical nanocrystals. Importantly, no Zn or Sn-related secondary phases were detected. Magnetic and optical techniques allowed us to gain comprehensive insights into the electronic properties of synthesised materials and their dependence on chemical composition. Building upon this foundation, we are currently working on the fabrication of CZTS nanoparticle-based solar cells and alternative post-deposition treatment, aiming to elucidate the intricate connection between device performances and the underlying chemical, structural, and electronic characteristics of kesterite materials based on nanoparticles.

The adopted analysis protocol allowed us to evaluate the stoichiometry of the products and their phase purity. Different amounts of Sn atoms were successfully incorporated into the crystallites, allowing us to unveil how the Sn concentration impacts both the paramagnetic defects and the plasmonic properties which are ultimately connected to charge carrier parameters, indicating a reduction in the free hole density in the lattice and a decrease of the bandgap as a function of Sn concentration. The presence of Cu2+–S bond was detected by Micro-Raman, thus we carefully analysed the magnetic properties of the produced material to clarify the nature of these impurities. We excluded the presence of CuS clusters inside the nanoparticle structure and noticed a moderate exchange interaction among differently oriented paramagnetic centres. Indeed, our synthetic method is simple and reproducible, paving the way for industrial scale-up and advancing towards the realization of next-generation kesterite solar cells.

METHODS TO CONTROL THE PHASE COMPOSITION AND TO TUNE THE LIGHT ABSORPTION PROPERTIES OF NANOMETRIC TiO_2 FOR SUSTAINABLE PHOTOCATALYTIC REACTIONS

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Throughout this century, climate change and the increasing energy demand have emerged as significant global concerns. TiO_2, thanks to its low toxicity and cost, has been extensively studied and employed as a photocatalyst to mitigate these challenges by exploiting (solar) light to produce fuels and chemicals. Various physicochemical factors influence its photocatalytic efficacy, including particle morphology, crystalline phases, band gap, and specific surface area. In this work, we have investigated the role of polymorphs. TiO_2 primarily exists in three more abundant crystalline phases: anatase, rutile, and brookite, each with distinct band gaps and electron-trap behaviours that impact photocatalytic performance. Additionally, to widen light absorption and facilitate photon delivery to catalytic sites, we have utilized copper-based QDs emitting in the NIR range as light-harvesting antennas.

Different titanium precursors, such as titanium tetrachloride and titanium tetraisopropoxide, were used to synthesize nanometric TiO_2. Sodium oxalate and sodium lactate, as chelating agents, and urea, as in situ OH^- source, were added to tune the polymorphs percentages. The pH was adjusted through nitric acid and the samples were calcinated at mild temperatures (below 650°C). Characterization of the studied nanomaterials has involved techniques such as X-ray powder diffraction (XRPD), quantitative phase analysis via Rietveld refinement, diffuse reflectance (DR) UV-Vis spectroscopy, N_2 adsorption/desorption, ζ-potential measurement for electrophoretic mobility in water, X-ray photoelectron spectroscopy (XPS), and electron microscopy. Photocatalytic performance assessment has been conducted under simulated sunlight at 1 Sun intensity (100 mW/cm^2).

By varying the chelating agents, the ageing time and temperature of calcination, we were able to control the amount of polymorphs and to obtain either single or multiphase nanocomposites, which were also successfully coupled with $CuInS_2$ quantum dots (CIS-QDS) to enhance their photocatalytic activities.

The presence of homo- and heterojunctions can affect the nanocomposites' photocatalytic performance. Preliminary chromatographic analyses for CO_2 reduction show a different amount of C1 and C2+ products based on the types of polymorphs present in the nanocomposite. Moreover, coupling TiO_2 with CIS-QDs can favour the conversion of dihydroeugenol to vanillin.

This study was carried out within the «GREEN UP: GREENER NANOMATERIALS FOR UPCONVERSION IN PHOTOCATALYTIC APPLICATIONS» project – funded by the Ministero dell'Università e della Ricerca – within the PRIN 2022 program (D.D.104 -02/02/2022) funded by the European Union - Next Generation EU. This manuscript reflects only the authors' views and opinions, and the Ministry cannot be considered responsible for them".

SYNTHESIS AND LUMINESCENCE STUDY OF MOCVD-GROWN Eu-DOPED BaF_2 THIN FILMS FOR ENHANCED ENERGY CONVERSION PHOTOVOLTAIC APPLICATIONS

Lo Presti F[1], Pellegrino AL[1], Milan E[2], Radicchi E[2], Speghini A[2], Malandrino G[1]

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In recent years, considerable research has been directed towards developing innovative functional materials tailored for the fabrication of advanced photovoltaic devices (PV), aimed at maximizing solar radiation efficiency. A cutting-edge strategy to enhance PV system efficacy involves converting photons with energies beyond the absorption range of the photoactive material into a more compatible optical spectrum. Lanthanide (Ln)-doped fluoride materials have emerged as highly promising candidates for energy conversion (EC) applications owing to their distinctive luminous properties when exposed to light irradiation. BaF_2 stands out among fluoride phases as a promising host for luminescent Ln^{3+} ions due to its low phonon energy, high stability, transparency, and diverse synthesis strategies. This study delves into the production process and luminescent properties of Eu-doped BaF_2 thin films fabricated using the metalorganic chemical vapor deposition technique (MOCVD).

For MOCVD deposition of pure and Eu-doped BaF_2 thin films, a multicomponent mixture of 'second generation' β-diketonate precursors was used as a single molten source. Depositions were conducted for 60 minutes at reduced pressure, with temperatures ranging from 300 to 600°C. The films were characterized structurally, morphologically, and compositionally using XRD, FE-SEM, and EDX. Finally, luminescence spectroscopy was used to evaluate the film functional properties.

Initial experiments were conducted on silicon substrates to confirm film purity, uniformity, and proper stoichiometry. The film chemical composition was adjusted by varying the precursor mixture to optimize the luminescence properties by controlling the Eu content. XRD patterns revealed the production of polycrystalline BaF_2 phase films within the 300 to 600 °C temperature range, with peak intensities generally increasing with deposition temperature due to enhanced film thickness and crystallinity. FE-SEM analysis showed that temperature influences morphology, with grain size increasing, up to 400 nm for samples deposited at 600 °C. The thin films exhibited strong Stokes luminescence when excited at the excited levels of Eu^{3+} ions. The emission band profiles varied with deposition temperature, suggesting slight variations in the local environment of the lanthanide ions.

Extensive research has been undertaken on producing Eu-doped BaF_2 thin films for EC applications. To ensure scalability and precise control over composition, microstructure, and morphology, an MOCVD approach has been adopted. These MOCVD-grown luminescent thin films hold great promise as downshifting layers in photovoltaic cells, allowing harnessing of the UV component of the solarspectrum.

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NOVEL PERYLENE DIIMIDE DERIVATIVES AS EFFICIENT LUMINOPHORES IN LUMINESCENT SOLAR CONCENTRATORS

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In the vast field of photovoltaic technologies, luminescent solar concentrators (LSC) offer a straightforward low-cost strategy to harvest, spectrally convert and optically concentrate solar photons providing an attractive solution for integrating photovoltaics into built environment and portable systems. The LSC's architecture consists of a thin plate of semitransparent material doped with luminescent dyes which act as a light guide. Their operating principle is simple: the dye absorbs both direct and indirect sunlight and re-emits it at lower energy; these photons, through total internal reflection, are concentrated at the edges of the device, where mounted PV cells convert light into electricity. Typically, the dyes are randomly dispersed in a polymeric matrix to form a thin film or a bulk slab. Thin film LSC configuration is to be preferred, as it allows to confine the total internal reflection mostly in a region where the dye is absent, reducing self-absorption phenomena. In addition, boosting the optical response of LSC allows to reduce energy losses, associated to non-radiative processes occurring within the device under operation, exploiting the Förster-resonance energy transfer (FRET).

The approach explored here is the covalent incorporation into the polymeric matrix of two well designed dyes with suitable absorption and emission spectra (for efficient FRET) in order to simultaneously broaden the absorption spectrum of the LSC device and reduce its self-absorption. For this purpose, two novel hydroxyl-functionalized luminescent molecules were synthesized, namely 4,7-di(4-hydroxymethyl-phenyl)benzo[c][1,2,5]thiadiazole (BTD) and 1,6,7,12-tetrakis(4-tert-butylphenoxy)-N,N'-(5-hydroxypentyl)-perylene-3,4,9,10-tetracarboxdiimide (PDI). BTD and PDI were then used, in different ratios, as chain extenders during the step-growth polyaddition reaction for the formation of linear luminescent polyurethane (PU) systems. The photophysics and PV response of the obtained LSC devices were deeply investigated.

The obtained PU systems demonstrated an excellent energy transfer efficiency (~90%) between the donor and acceptor moieties. The corresponding LSC devices showed an outstanding photonic response, with external photon efficiency reaching up to ~4% and internal photon

The applicability of our novel PU materials in the area of highly transparent spectral conversion devices was demonstrated. Their optimized power conversion efficiency combined with their enhanced average visible light transmittance highlighted their suitability for transparent solar energy devices. These results represent the first example of LSCs exploiting the FRET mechanism through direct in-chain incorporation within luminescent polyurethane matrices. They have an appealing new route for building-integrated PV applications.

LITHIUM-ION BATTERY ANODES BASED ON $(Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5}Zn_{1/5})_3O_4$ NANOFIBERS: CHARGE STORAGE MECHANISM

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Spinel-type high-entropy oxides (SHEOs) are promising anode materials for next-generation lithium-ion batteries (LIBs). In this work, $(Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5}Zn_{1/5})_3O_4$ SHEO nanofibers (NFs) are produced under environmentally friendly calcination conditions and evaluated as anode active material in LIBs. The NF properties and Li^+-storage mechanism are thoroughly investigated by several analytical techniques, including ex situ synchrotron x-ray absorption spectroscopy (XAS).

The SHEO-NFs are prepared by electrospinning and calcination in air at 700°C for 2h. To evaluate their electrochemical behaviour in CR2032-type coin cells, the anode is prepared by homogeneously mixing NFs, Super P carbon black and polyvinylidene fluoride in mass ratio 7:2:1 with N-methyl-2-pyrrolidone.

Ex-situ analyses on the discharged anodes at different state of charges reveal that charge storage occurs through lithium insertion, cation migration, and metal-forming conversion reaction. The process is not fully reversible and the reduction of cations to the metallic form is not complete. Iron, cobalt and nickel, initially present mainly as Fe^{3+}, Co^{3+}/Co^{2+}, and Ni^{2+}, undergo reduction to Fe^0, Co^0 and Ni^0 to different extent (Fe < Co < Ni). Manganese undergoes partial reduction to Mn^{3+}/Mn^{2+} and, upon re-oxidation, does not revert to the pristine oxidation state (+4). Zn^{2+} cations do not electrochemically participate in the conversion reaction, but migrate from tetrahedral to octahedral positions, leading to a phase transition from spinel to rock-salt.

OPERANDO STUDY OF COBALT-ALUMINUM LDH FOR OXYGEN EVOLUTION REACTION

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The over-exploitation of fossil fuels intensifies environmental concerns, driving the search for a cleaner and sustainable energy infrastructure infrastructure. Among the innovative solutions, one is "Green hydrogen" obtained from water electrolysis However, w hile electrocatalytic water splitting holds promise for sustainable hydrogen production, the prohibitive cost of traditional electrocatalysts, such as precious and critical metal oxides, remains a major obstacle. This has led to the exploration of transition metal-based catalysts, such as oxides/hydroxides nanoparticles and layered double hydroxide (LDH), due to their activity, abundance, and stability under alkaline conditions. The focus of th is presentation is on the electrocatalyst CoAl LDH, specifically studied for the oxygen evolution reaction (OER).

CoAl LDH was synthesized via a hydrothermal method using nitrates and urea. The material was tested for OER in a three-electrode cell under alkaline conditions. Morphological and compositional analyses were conducted using Transmission and Scanning Electron Microscopy (TEM, SEM) and synchrotron radiation spectroscopy (at BACH beamline, Elettra), including x-ray photoemission spectroscopy (XPS) and near edge x-ray adsorption fine structure (NEXAFS). Operando NEXAFS was performed during OER.

Physical-chemical characterizations confirm that CoAl LDH mirrors the structure of $Co(OH)_2$, with octahedrally coordinated Co with substitutional Al, and a homogeneous distribution of Co:Al in a 3:1 ratio. In electrochemistry it exhibits a distinct activation trend with increasing activity in the OER range. This enhanced activity is attributed to the leaching of Al and recrystallization in $Co(OH)_2$/CoOOH, as revealed by operando measurements that also proved a unique redox behaviour.

Despite the apparent similarity to $Co(OH)_2$, especially after the loss of Al, CoAl LDH exhibits distinct features in operando conditions. In the well-studied case of $Co(OH)_2$ scanning the potential anodically, Co transitions from 2+ to an intermediate hydroxide intercalated state (oxidation state of 2.5+), to reach 3+ during OER. However, for CoAl LDH, the contact of alkaline electrolyte at open-circuit potential (OCP) induces a 2.2-2.3+ oxidation state, transitioning to 3+ during OER. Interestingly, upon returning to OCP conditions the material, i.e. after Al leaching, it stabilizes at 2.5+, without regressing to 2+. We attribute the unique redox behaviors to the atomic loss of Al, causing a noticeable increase in grain boundaries. This increase not only enhances the OER activity but also appears to alter the material's overall chemical state. Operando NEXAFS proved to be crucial for a comprehensive understanding, as pre- and post-catalysis analyses offer limited insights into real operating conditions.

ROLE OF SURFACE IR-OXO SPECIE IN TUNING MOLECULAR OXYGEN EVOLUTION ELECTROCATALYSIS BY IRIDIUM OXIDE: NEW INSIGHTS FROM MULTIREFERENCE CALCULATIONS

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Understanding the mechanisms driving the oxygen evolution reaction (OER) is essential for achieving an efficient scale-up of Iridium Oxide (IrO_2)–based catalysts. The OER mechanism has been widely addressed using density functional theory (DFT). After the formation of a Ir-oxo species on the surface, the proposed mechanism for the oxygen release is the adsorbate evolving mechanism (AEM). Nevertheless, due to the known over-binding of oxygen by standard GGA functional, DFT predicts a too high barrier for removing O_2. In this contribution, we address the formation of O_2 from the most stable (110)-IrO_2 surface and compare periodic DFT with an embedded cluster approach (EEC) at the multireference NEVPT2 level of theory.
We report a study on oxygen release from the most stable stoichiometric IrO_2(110) surface by means of EEC based on NEVPT2 level of theory (EEC[NEVPT2]). A small cluster of atoms, where the localized chemical processes occur, is described at NEVPT2 level of theory, while the extended chemical surface environment is simulated through a point charge field, as implemented in ORCA.
Such embedding approach can predict an energy barrier consistent with the previous derived microkinetic value. Analysis of electronic features suggests that such barrier is related to a significant O_2 interaction with adjacent electrophilic Ir-oxo specie, which is present under experimental operating conditions. Overall, our study highlights the potential of embedding methods beyond standard DFT for unveiling complex reactions at heterogeneous electrocatalytic interfaces.
Periodic DFT calculations at PBE level of theory predicts a high energy barrier (~1.10 eV) for dioxygen release via the AEM path. Because this step involves radical Ir-oxo specie and triplet O_2, EEC[NEVPT2] approach is used to provide a reliable electronic description of this process. We validate this method analyzing different clusters and charge arrays of increasing size at PBE level of theory. Energetic and electronic analysis reveals that the smaller cluster with 2 Ir atoms with the largest charge array is the best choice to mimic the periodic IrO_2(110) surface at affordable computational costs. Plus, large active spaces are required for the convergence to the final energetics. The activation energy at NEVPT2 level of theory (0.50 eV) is consistent with the derived microkinetic value (0.43 eV). By analysis of the active orbitals, such a barrier can be ascribed to the breaking of a π interaction between O_2 and Ir surface atom, and of a further interaction with adjacent electrophilic Ir-oxo species.

FUNCTIONALIZATION OF SILICA WITH AMINES BY MEANS OF SUPERCRITICAL CO_2

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Carbon sequestration is among the different strategies investigated to reach climate change mitigation. The dominant technology currently used for carbon sequestration relies on adsorption by liquid amines, although liquid amines present problems of corrosion and require high energy for regeneration. Thanks to their ease of use and regeneration, solid sorbents represent an interesting alternative. In this work we investigate the possibility of obtaining a solid sorbent made of amine-functionalised mesoporous silica prepared through a green process involving the use of supercritical CO_2 ($scCO_2$) as a solvent.

(3-aminopropyl)triethoxysilane (APTES) and 1,6-diaminohexane (DH) were loaded on a commercial mesoporous silica SBA-15 by $scCO_2$ impregnation. The samples were characterized in terms of physico-chemical properties by means of Fourier Transform Infra-Red Spectroscopy (FTIR), X Ray diffraction, Thermogravimetric analysis (TGA), nitrogen adsorption. In addition, the adsorption of CO_2 on the samples was evaluated by CO_2 adsorption volumetric measurements and in-situ FTIR at room temperature.

FTIR and TGA results confirm that the $scCO_2$ impregnation process is successful in loading both amines on the SBA-15 silica support. Although APTES is expected to bond covalently to the silica surface, while DH is expected to interact only by means of intermolecular interactions, both amines result stable at 120 °C, i.e. at a temperature comparable to that of the regeneration process. Volumetric test and in-situ FTIR analysis show that the functionalised supports are particularly effective in adsorbing (also in a specific way) CO_2 at low pressure.

On the overall, this study shows that it is possible to obtain amine-functionalized silica sorbents exploiting the solvent properties of $scCO_2$ instead of recurring to the use of polluting organic solvents. The obtained solid sorbents present encouraging properties in view of a possible application in carbon sequestration, with particular interest in applications where CO_2 partial pressure is low.

BLENDS OF POLYLACTIC ACID WITH BIOBASED, CHEMICALLY RECYCLABLE, AND SELF-HEALABLE THERMOSET

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The replacement of heavier steel components with lighter polymer counterparts is a major challenge in automotive industries because it allows for improved vehicle performance and reduced CO_2 emissions. Thermosets are the most lightweight and cost-effective option due to their highly rigid and crosslinked structure; however, traditional ones have sustainability issues, due to being petrol-based and not recyclable or reparable. These issues can be solved by designing biomass-derived thermosets incorporating reversible covalent bonds, such as imine functions, into the network. Thermosets can be employed in blends with thermoplastics to enhance their mechanical and thermal properties. In this work, the combination of a biobased thermoplastic polymer, i.e. poly(L-lactic acid) (PLLA), with a bio-based and self-healing Schiff-base vanillin thermoset is investigated to obtain advanced lightweight material.

Vanillin, methacrylic anhydride, 4-(dimethylamino)pyridin, 1,8-diamino-3,6-dioxaoctane, sodium bicarbonate, sodium hydroxide, 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959), dichloride methane (DCM), and dimethylformamide were purchased by Sigma-Aldrich and used for the synthesis of the resin. Poly(L-lactic acid) (PLLA) was purchased by Mitsui Fine Chemicals. Films of thermoplastic-thermoset blends were produced by solvent casting from DCM, while nanofibrous mats were obtained by electrospinning PLLA+resin solution in the presence of the photo-initiator. UV curing (UV lamp Thorlabs, $\lambda = 365$ nm) was carried out on both films and electrospun mats. TGA was carried out using a TGA Q500 thermogravimetric analyzer (TA Instruments). Thermal transitions were investigated using a TA Instruments DSC Q2000. SEM observations were performed on gold-sputtered mats. Solubility tests have been performed by sample immersion in DCM. Mechanical properties were investigated by means of a Dynamic Mechanical Analyzer, Q800 T.A. Instrument.

The resin was successfully synthesized through a two-step process, involving the methacrylation of vanillin followed by its subsequent Schiff-base reaction with the 2,2-(ethylenedioxy)bis(ethylamine). The resulting resin was characterized by the presence of two imine bonds, along with two vinyl functions exploitable for the curing. The blends at different compositions (PLLA/resin 80/20, 50/50, 20/80) were produced in the form of films from solvent casting, and in the form of electrospun mats. An optimized curing process, consisting in the combination of UV light and a thermal post-treatment. was identified for the resin and blends. Thermal and mechanical properties of films and electrospun mats were characterized and compared.

The results demonstrated the possibility of producing bio-based blends of PLLA and a Schiff-base vanillin thermoset. The morphology and thermo-mechanical properties of the blends are correlated to blend composition. Further research is ongoing to study the self-healing properties of the blends and their chemical recyclability.

ENHANCING PHOTOELECTROCHEMICAL PERFORMANCES OF FTO SUBSTRATES WITH METAL-ORGANIC FRAMEWORK FILMS

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The versatility of Metal-Organic Frameworks (MOFs) has positioned them as pivotal in photoelectrochemical applications, with their performance optimization being a key research focus. This study explores the enhancement of photoelectrocatalytic properties through the modification of FTO substrates with single-metal (Bi) and bimetallic (Bi and Eu) MOFs, using 2,6-naphthalene dicarboxylic acid as the ligand. We investigate both traditional deposition methods and direct MOF growth on substrates for film creation, aiming to improve the Oxygen Evolution Reaction (OER) photoelectron activity.

Bi-NDC and BiEu-NDC MOFs were synthesized at 120°C via a reflux process, later functionalized with polymers such as Polyethylene Glycol (PEG) and Polyvinylidene Fluoride (PVDF) to enhance water dispersibility and binding for drop casting. Additionally, a multi-step approach involving FTO prefunctionalization with a phosphonic linker, followed by MOF formation from $Bi(NO_3)_3$ and H2BDC precursors, facilitated thin film growth. Morphological and chemical analyses were performed using XPS, SEM, and FT-IR, while electrochemical properties were assessed through Cyclic Voltammetry and linear sweep voltammetry, under both dark and visible light conditions. Modified FTO substrates with Bi-NDC and BiEu-NDC exhibited marked electrochemical performance enhancements over unmodified FTO. Notably, the electrochemical surface area (ECSA) of MOF-modified electrodes was 3-4 times larger than that of bare FTO. The modified electrodes also demonstrated superior OER efficiency in 0.1M NaOH, evidenced by lower overpotentials and improved Tafel plot slopes. This performance boost is attributed to the increased active surface area and the facilitation of electron transfer by the MOF structure and Europium doping. Moreover, under visible light illumination, Bi and BiEu-NDC MOFs showed enhanced OER activity, underscoring the potential of MOF-functionalized substrates in advancing sustainable energy production technologies.

COPPER-BASED PHOTOELECTRODES DEVELOPMENT FOR HYDROGEN PRODUCTION

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Copper has been inserted in the strategic list of raw materials by the European Union. The main reason is ascribable to the large demand of copper in Solar X technologies and its wide availability in Western countries. Altogether these aspects render Cu a suitable material for large scale application of copper-based materials also in the photoelectrochemical hydrogen production, by the realization of cheap photoelectrodes (both cathodes and anodes) with tunable and beneficial optoelectrochemical properties.

Exploiting wet-chemical approaches like hydro/solvothermal technique at low temperatures and laser-ablation assisted in liquid coupled to ultrasonic spray coating it is possible to prepare thin films with modulated thickness of Cu_2O and $CuWO_4$. In addition, the latter will be doped with Fe^{3+} cations, for improving the catalytic properties. A detailed functional and structural characterization is provided.

The Cu_2O displays suitable performances for hydrogen production, as well the $CuWO_4$ (both doped and undoped) for oxygen evolution reaction. Particularly interesting are the results concerning the advanced characterization applied: by means of EPR and IMPS (intensity modulated photoelectron spectroscopy) the nature of dopants will be investigated.

Cupreous oxide photoelectrochemical properties are strongly affected by physical treatments that allow the substrate to improve its durability in water environments during use. An innovative mechanism of self-healing of the Cu_2O is presented and discussed in detail. The $Fe:CuWO_4$ photoanodes, on the other hand, unveil improved OER (of the order of 3 times) due to a particular rearrangement of the atoms that positively affects the hole mobility of the anode: we speculated a mechanism occurred during the iron doping by the synergetic results of EPR, photoluminescence and IMPS.

MULTIPURPOSE ELECTRODE FOR SYMMETRIC CO_2-SOECS

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The development of a Co- and Ni-free electrocatalyst for carbon dioxide electrolysis would be a turning point for the large-scale commercialization of solid oxide carbon dioxide electrolysis cells (CO_2-SOEC). Indeed, the demand of cobalt, nickel and other transition metals is expected to grow rapidly and become critical by 2050 due to the automotive electrification. Currently, the reference materials for electrodes are perovskite oxides containing Mn or Co for anodes and Ni-YSZ cermets for cathodes. However, some problems still need to be addressed such as microstructural cracking due to the evolution of pressurized oxygen molecules at the anode side and structural degradation and/or carbon deposition at the cathode side especially in presence of high overpotentials (above ± 1.8 V).

This work designs the 20 mol% replacement of iron by copper in $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ as a multipurpose electrode for symmetric CO_2-SOECs. $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSFCu) is synthesized by solution combustion method, and the lattice modification introduced by copper substitution into LSF is evaluated by XRPD and the spectra are analyzed by Rietveld refinement. The oxidation states of Cu and Fe ions are investigated by X-ray photoelectron spectroscopy (XPS).

LSFCu is initially tested as a SOEC air electrode by measuring the electrical conductivity versus temperature and the area-specific resistance (ASR) versus T and pO_2. Then, the structural, electrical, and electrocatalytic properties of LSFCu are measured in pure CO_2. Temperature-programmed CO_2 desorption is employed to evaluate the chemical affinity of LSFCu to carbon dioxide. Finally, the proof of concept of a symmetric LSFCu-based SOEC is tested at 850 °C for CO_2 electrolysis, revealing a current density value at 1.5 V of 1.22 A/cm^2 which is higher than Fe-containing perovskite-based electrodes similar systems. LSFCu-based SOEC also reveals a fast and constant response to different applied voltages, and a long-term resistance in galvanostatic mode almost without any cell degradation (+5.8% increase in cell voltage) after 150 hours.

A PERFLUORINATED MIL-140A(CE)-BASED MIXED MATRIX MEMBRANES FOR CO_2 CAPTURE

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Membrane technology for gas separation represents a potential solution and a growing field with a focus on developing advanced membranes to capture CO_2. The efficiency of the separation processes can be achieved by exploiting the advanced mixed matrix membranes (MMMs) based on the combination of a polymeric matrix with crystalline porous fillers such as metal-organic frameworks (MOFs). The fluorinated-MOFs in combination with perfluoropolymers represent membranes able to exhibit a good compromise among the permeability of the fast gas of a gas pair and their separation factor.

Molecular modelling is used to investigate the potentiality of a novel per-fluorinated Ce(IV)-based MOF with MIL-140A topology for CO_2 capture in dry and hydrated conditions. MD simulations are carried out to analyze the CO_2 adsorption capability of MIL-140A(Ce) at 273K and 1 bar using the Grand Canonical Monte Carlo method. Investigations on the adsorption sites of the MIL-140A(Ce) are supported by the study of the pore size distribution and the radial distribution functions. Dense MMMs are prepared by loading the 20 wt% of F4_MIL-140A(Ce) on the total solid in Hyflon®AD60X solution. The transport properties of the mixed matrix membranes are investigated by pure-gas permeation tests.

A good comparison of the simulated adsorption isotherms to the experimental data is found for MIL-140A(Ce) at 1 bar and 273 K. The definition of the available void space gives the identification of the most populated channels and the dimensionality of the voids. The incorporation of F4_MIL-140A(Ce) into the Hyflon®AD60X leads to an improvement in selectivity for CO_2/CH_4 and CO_2/N_2 gas pairs. Pure-gas permeation tests on MMMs confirmed the enhancement of selectivity for CO_2/N_2 and CO_2/CH_4 gas, with no significant reduction in permeability.

The CO_2 adsorption mechanism defines the accessible sites for the adsorbate molecules of MIL-140A(Ce), obtaining an open-site cerium-CO_2 coordination in the dry MIL140A(Ce), and the adsorption of the CO_2 in a specific environment in the hydrated MIL-140A(Ce). The interactions between MIL-140A(Ce) and CO_2 are defined by the specific pore sizes and the electronic properties. The addition of the F4_MIL-140A(Ce) in the Hyflon®AD60X leads to obtain the uniform dispersion of the MOF in the matrix. The transport properties of the developed mixed matrix membranes at 25°C confirmed the enhancement of the selectivity of CO_2/N_2, and CO_2/CH_4 gas and of permeability, justified by the good compatibility among the specific CO_2-philic and the highly polar fluorine atoms.

ADSORPTION PROCESSES IN METAL-ORGANIC FRAMEWORKS: IN SITU INSIGHTS FROM COMBINED X-RAY TECHNIQUES

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To develop and optimize novel adsorbents exhibiting selective metal–adsorbate interactions or specific guest-adsorption, and to deeply characterize their crystal structure, electronic and oxidation/charge states, it is crucial to elucidate the role of coordinatively unsaturated metal centres, specific adsorption sites and key physical changes upon guest binding. To this aim, the combination of in situ and operando crystallographic and spectroscopic techniques is becoming essential to rationalize and understand the metal-organic frameworks' structure vs. function relationships, demonstrating that a multi technique approach can reveal unprecedented details about the underlying processes.

My research group is working in the direction of deeply understand the structural changes in long-range order and local environment during adsorption processes and catalysis utilizing in situ X-ray diffraction and operando (hard and soft) X-ray absorption experiments, or a combination of both. This includes the synthesis of novel adsorbent MOF materials, the rationalization of gate-opening effects and cooperative gas adsorption phenomena, and the understanding of key active sites during adsorption and catalysis.

In this lecture, I will present our recent results, obtained using a combination of techniques (even custom-made), through the description of recent key studies, such as: i) in-situ detection of specific adsorption sites for CO_2 adsorption in humid conditions; ii) combined XAS/PXRD experiments for the description of long-range and local structure evolution during water harvesting and iii) in depth analysis of ‘PXRD CO_2 adsorption isotherms’, including retrieval of heat of adsorption, and host-guest interactions through ab-initio structure solution and Rietveld methods.

COMPUTATIONAL STUDY OF THE IMPACT OF AMINOPROPYL UNITS ON PHYSISORPTION OF CO_2 AND CH_4 IN MESOSTRUCTURED SILICA

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Mesoporous silica-based materials are of significant interest for applications like capture, storage, and catalysis due to their large surface area, uniform pore distribution, and customizable surface chamistry. MCM-41, with its 2D hexagonal pore symmetry, serves as an ideal model. This computational study explores the introduction of aminopropyl groups to enhance CO_2 adsorption in CO_2/CH_4 mixtures, investigating the interplay of factors affecting overall performance, including the pore size. The research focuses on shedding light on the microscopic details underlying the physisorption of CO_2 and CH_4, offering insights into enhancing adsorption capacity and selectivity, crucial for optimizing these materials in diverse applications.

Three silica-based material models with different pore size were prepared by using all the available experimental information of real reference samples. By using an in-house code, aminopropylsilane (APS) functional units were randomly introduced on pore surface, ensuring the same surface concentration. The study involved equilibration of the material and gas adsorption simulations using a combination of Grand Canonical Monte Carlo and Molecular Dynamics methods. State-of-the-art force-field parameters were used. A detailed analyses of the trajectories was performed, comprising gas density profiles, azimuthal position distribution, radial distribution functions, adsorption capacity and selectivity, and diffusion coefficients, to provide a comprehensive understanding of the materials' performance at the microscopic level, which is difficult to achieve with experiments.

In this study, the impact of APS functionalization on gas adsorption in silica-based materials was investigated. CO_2 consistently showed higher affinity than CH_4, but APS units altered CH_4 adsorption more than CO_2. The smallest and largest pore size materials exhibited increased CH_4 affinity after APS-functionalization. Selectivity for CO_2 over CH_4 was still evident, but the changes did not correlate with surface area. The intermediate pore size material showed superior overall performance.

The microscopic analysis of simulation trajectories reveals that CO_2 preferentially physiosorbs on silanol groups, emphasizing their role in CO_2 capture and bolstering their assiting role in chemisorption by the aminopropyl chains. Moreover, amino groups compete with CO_2 for interacting with silanol, while the propyl chains enhance CH_4 affinity by creating niches where CH_4 can favorably interact with the methylene groups. These effects, linked to alkyl chain density and pore curvature modulate material selectivity. Intermediate pore size optimally balances these effects, resulting in the best performance.

THE DANTE PROJECT: THE INSTM-ENI COOPERATION FOR CO_2 CONVERSION TO E-FUELS THROUGH AN INNOVATIVE APPROACH

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DANTE project aims to develop an innovative technology for CO_2 direct capture from emissions and its integrated conversion to e-fuels by using renewable energy and water with a highly energy-efficient solution based on decoupling anodic and cathodic reactions in an electrocatalytic device. In addition to cell and electrode design, the key feature of the proposed DANTE technology is the use of a tailored innovative membrane at the surface of a gas-diffusion electrode allowing the direct capture and concentration of CO_2 at the electrocatalyst surface (avoiding thus a separate step of CO_2 capture and concentration), which is integrated, converted to efuels in the presence of protons/electrons produced from water. By decoupling the anodic reaction of oxygen evolution reaction by using advanced 3D-type anodes, it is possible to increase the efficiency close to the thermodynamic limit.

By combining the directly integrated solution of CO_2 capture with the highly efficient electrocatalytic conversion, all based only on the use of renewable energy sources, the DANTE project proposes a unique solution to achieve at the same time a carbon-negative impact in CO_2 reduction and low Capex/Opex costs with the valorisation of CO_2 to produce e-fuels as methane. The project will develop the materials needed for these novel solutions (membranes, electrocatalysts, electrodes), the cell design and engineering, integrating all the components in a small-scale device prototype to prove the concept and allow its assessment as the basis for further development at higher TRLs.

It is a disruptive innovation that combines many interdisciplinary competencies to succeed. INSTM offers a unique possibility to be the single-entry point to gather the best excellences in Italy to work in synergy on this highly challenging topic. In the DANTE project, Messina, Salerno, Torino, Milano-Bicocca and Padova research units will work together to develop this novel technology.

ENI and PNRR are supporting five PhD positions through the International and Industrial Doctorate Course ACCESS (Advanced Catalytic Processes for Using Renewable Energy Sources) of the University of Messina, coordinating the project. The PhD students started activities by the end of Dec. 2023.

The lecture will introduce the project concepts and their scientific/technical novelty, evidencing how this project is a valuable case example of the INSTM cooperation with ENI SpA and can be a model for the role of the Consortium in gathering multiple competencies to address the need of companies while promoting educational activities and the role of the Universities participating to the Consortium.

CO_2 CONVERSION THROUGH CARBONATION OF SILICATE BASED SYSTEMS INDUCED BY MECHANICAL TREATMENT: REACTIVITY AND KINETIC FEATURES

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Within the framework of CCUS, (Carbon Capture Utilization and Storage) strategies, the development of innovative materials and chemical processes plays a key role in view to the set-up of large-scale applicable technologies, aimed to mitigate the rise of CO_2 concentration in the atmosphere. To this regard, carbon mineralization processes offer, at least in principle, an interesting route for CO_2 conversion over different classes of materials and mineral substrates, that is even observable in natural context although characterized by sluggish kinetics. Solid-gas interactions can be effectively tuned by the use of mechanical energy, and it appears of particular interest in industrial processes involving mechanical treatment.

In the present work we, then, focus on the mechanochemical activation of the CO_2 conversion process: different classes of silicate-based materials, including minerals, pure systems, and industrial slags, were subjected to mechanical treatment in presence of H_2O, under CO_2 atmosphere. Suitably modified ball milling vials were used as mechanochemical reactors, operating under continuous flow of gaseous reagents.

Attention has been paid both to the structural evolution of the solid phases towards carbonation products, and to the CO_2 reduction to methane and light hydrocarbons. Chemical reactivity and reaction rates were investigated by resorting to different instrumental techniques and under different experimental conditions with the aim to gain knowledge of reaction mechanism details.

GREEN FUNCTIONALIZATION OF TORREFIED BIOMASS VIA MECHANOCHEMICAL APPROACH: NEW OPPORTUNITIES FOR FILLER PRODUCTION

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Biochar's physical-chemical properties and yields are both influenced by the feedstock and the operating pyrolysis variables. At temperatures lower than 300°C pyrolysis is referred to as torrefaction, and the solid residue is defined as torrefied biomass.

Although biomass derivatives have received growing attention as renewable sources for several applications such as removing pollutants, remediating soil, and reducing greenhouse gas emissions, recently, considerable attention was paid to them as a filler for polymer. To better affect the polymer properties, good filler dispersibility can be realized by using nanometric particle size and physical interactions between the filler and the polymer matrix.

Torrefied biomass and biochar derived from Populus Nigra were produced in a fixed-bed reactor with a flexible configuration to tune the main torrefaction and pyrolysis parameters. The experiments were conducted at a constant flow of nitrogen under slow heating up to the final temperature of 285 °C and 450 °C. The torrefied biomass and the biochar samples were labeled B1 and B2 respectively and were mixed with Dodecyl triphenyl phosphonium bromide (DTPPBr), and ground for 30 minutes at 300 rpm.

B1 and B2 were characterized by Elemental Analysis, TGA, WAXD, FTIR, and BET. FTIR showed the chemical nature of the functional groups after low and high-temperature pyrolysis, highlighting the significant differences in oxygen functionalities between B1 and B2, mainly regarding the hydroxyl ones. Then, to verify the ability of B1 to be ionically functionalized by using the mechanochemical approach, the reaction was performed by mixing B1 and DTPPBr and milling at 300 rpm for 30 minutes. The product B1/DTPP, nanometrically reduced, was homogeneously dispersed on cotton fabrics, and its photocatalytic ability was successfully tested.

A green and sustainable functionalization of the torrified biomass B1 treated at low temperature (T= 285 °C) with a mechanochemical approach is realized.

The reaction is performed in the presence of DTPPBr to produce a new filler with antimicrobial activity. By selecting the right thermal treatment, oxygen functionalities can be obtained on the carbon surface, avoiding the additional oxidation step to further modify the carbon material. In a one-step procedure, the filler is nanometrically reduced and is properly functionalized via cation exchange in a short time in dry conditions, providing a salt uptake of about 15 wt%. The new adduct exhibits high dispersibility on cotton fabrics and shows photocatalytic activity which confirms the capability of the manufacture to inhibit the organic contaminants' growth.

WASTE-BASED HYDROGELS FOR ENVIRONMENTAL AND AGRICULTURAL APPLICATIONS

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For most industrial processes waste is an unavoidable by-product that strongly impacts on their environmental sustainability, safety, social and economic return. In this presentation, we will show some examples of recovery and reuse of both food and industrial waste for generating new classes of smart multifunctional materials for environmental remediation, in particular water and air purification and their extension as bio-stimulants for horticulture. The rationale of this approach leverages on the synergistic combination of different units, each one made of waste-based materials, which can either efficiently capture, detect and remove several classes of environmental pollutants, including pesticides, drugs, heavy metals and polychlorinated biphenyls or elicit self-protection mechanism in plants.

The smart hydrogels were based of chitosan extracted from household shrimp shells. Depending on the final application, these hydrogels were combined with different additives, including iron mill scale derived from industrial waste.

The wasted-derived hydrogels were successfully tested for adsorption and removal of different classes of environmental pollutants, such as organic dyes, pharmaceutical compounds, endocrine interferents and heavy metals. In most of the cases the combined action of scavenging and catalytic activity of the smart hydrogels allowed for the complete removal of the organic pollutants. Heavy metals were totally recovered and reintegrated in the production of value-added materials. Chitosan-based nanoparticles were also successfully tested in protection against Tobacco Necrosis Virus (TNV).

These results demonstrate the disruptive concept of waste-aided environmental remediation, highlighting the importance of symbiotic approaches for integrating chemistry in circular systems to produce sustainable materials.

PVDF-BASED MICROPOROUS LAYER BY PHASE INVERSION TECHNIQUE USING GREEN SOLVENTS

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Diffusion layers (DLs) play an important role in electrochemical devices by distributing the reactants (e.g. in fuel cells) over the catalytic layers, collecting products (e.g. in electrolyzers) and providing the necessary electrical conductivity to transfer the electrons to the flow field current collectors. A diffusion layer is usually constituted of a microporous layer (MPL) supported by a carbon substrate as well as a carbon cloth or a carbon paper. For low temperature fuel cell applications, one of the requirements of the MPL is to be hydrophobic to easily expulse liquid water. In our previous studies we have proposed polyvinylidene difluoride (PVDF) as hydrophobic binder which allow to achieve a more accurate control of the microporous structure of the MPL by adopting the nonsolvent induced phase inversion technique (NIPS) which is well-known for the preparation of porous polymeric membranes. In this work, either dihydrolevoglucosenone or triethyl phosphate were explored as a green solvent to prepare electrically conductive MPLs.

PVDF was dissolved in the green solvent (e.g. dihydrolevoglucosenone or triethyl phosphate) before the addition of carbon black as electrically conductive filler and a non-solvent as water or ethanol were used to precipitate the MPL. The influence of polymer/filler ratio and coagulation bath conditions on the characteristics of the MPLs was thoroughly analyzed. The MPLs were characterized in terms of contact angle, roughness, morphology by optical and electron microscopy, porosity, pore size distribution, in-plane and through-plane electrical conductivity, and through-plane air permeability. The performance of the MPLs was proved in a PEMFC fed with hydrogen and air at room temperature.

The prepared PVDF MPL films were investigated with surface roughness of above 2 μm and high contact angle of above 135°. While the electrical conductivity increased by increasing the carbon black content, the air permeability was more dependent on the particular porous structure induced by the introduction of the filler. The PVDF MPLs showed an improving performance at higher carbon filler content.

In the PVDF/dihydrolevoglucosenone /Water system, the higher the concentration of PVDF in solution, the smaller the water required for inducing the de-mixing process. The morphology of PVDF-based films was obtained with spherulitic microparticles linked through fiber-like connection. The obtained porous structure was effective in distributing the reactants while obtaining a electrical conductivity remains of paramount importance.

DEEP EUTECTIC SOLVENTS ASSISTED GROWTH OF MAGNETIC NANOPARTICLES: A CORRELATION STUDY

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Deep eutectic solvents (DESs), like an alternative type of ionic solvents to classical Ionic Liquids, have emerged as particularly promising candidates for organic synthesis due to their ability to dissolve both polar and non-polar reactants and their facile recovery. Initially reported in the early 21st century by Abbot and colleagues, DESs entail the combination of quaternary ammonium or phosphonium salts with an organic compound typically containing hydrogen-bond donor groups. The physicochemical properties of deep eutectic solvents (DESs) depend on the selected combination of hydrogen bond acceptors and hydrogen bond donors used. Another possibility for the use of DESs is the processing of metals, based on the ability to solvate a wide range of transition metal species, including metal oxides and hydroxides, without the highly acidic conditions that are needed in analogous aqueous systems. Extensive studies have been performed on the solubility of metal oxides in a variety of deep eutectic solvents.
With the aim of seeking to analyse the role, if any, played in the growth of magnetic nanoparticles, in this study, we opted to synthesize magnetic nanoparticles in various DESs to investigate how their nature, particularly in the terms of tunability of their acid-base properties, influences the magnetic properties and morphology of the nanoparticles.
For the synthesis of nanoparticles in DES, we decided to employ the hydrothermal method, previously optimized in our laboratory. In this method, the use of a base is necessary. Therefore, to determine which DESs to synthesize, we considered the basicity of the two main components constituting the DESs. Specifically, we selected two hydrogen bond acceptors, namely choline chloride and guanidine chloride. Overall, we synthesized six DESs using hydrogen bond donors having different acid-base properties, ranging from two basic donor like urea and guanidine, a neutral donor, triethylene glycol and an acidic donor, as gallic acid. After selecting donors and acceptors, the reciprocal ratios were optimized to obtain the DESs, which have been full characterized.
Preliminary results confirmed that magnetic properties of nanoparticles, that is a competition between magnetite or hematite phases of ferrite, are affected by the different nature of DESs.
Anyway, a full correlation between the physicochemical properties of DESs and the physical and chemical properties of synthetized nanoparticles (in terms of size, morphology, surface, and intrinsic properties), will be given in this presentation.

ENHANCING THE BIODEGRADATION KINETICS OF PLA USING HEMP SHIVE FIBERS

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Biodegradable polymers are polymers able to undergo biological degradation by living organisms down to the base substances (water, carbon dioxide, methane, basic elements and biomass) in "short times". A standard for biodegradability used by the European Union is that >90% of the original material must be mineralized within 6 months. According to this definition, PLA is not biodegradable as it needs longer time to degrade in soil or water. To accelerate the process, we added natural fibers to transport water from the external environment, thus favouring hydrolysis, which is the limiting step of PLA biodegradation.

PLA (Luminy® LX175 by Corbion) was melt compounded with 5 to 30 vol.% of hemp fibers (Equilibrium Srl). Degradation in freshwater and soil were monitored. Characterizations included optical and scanning electron microscopy, Size Exclusion Chromatography (SEC), and Differential Scanning Calorimetry (DSC).

The impact of short hemp fibers on the degradation of PLA in freshwater (T=45°C) and soil (T=55°C) was studied, with a focus on fiber content and PLA crystallinity. The fibers accelerated the rate of molecular weight decrease in water, while contrasting effects were found in soil (acceleration of the degradation rate at short times, followed by a deceleration).

When the samples are immersed in water, the hemp fibers facilitated water access promoting hydrolysis and accelerating PLA degradation, especially above the percolation threshold (10 wt.%). The swelling of the wet fibers and the weak fiber-matrix interface likely created water-rich pockets, contributing to this process. Differently, when the samples are buried in soil, after an initial hydrolysis acceleration in the first 10 days, the fibers slowed down the degradation kinetics because of a shielding effect of fiber-induced crystalline domains, which limited water diffusion preserving the amorphous PLA from being hydrolysed. Nonetheless, the samples buried in soil degraded much faster than those immersed in freshwater (full degradation in <50 days) due to the different temperatures of the two treatments. The temperature hence confirms to be one of the most critical parameters to promote PLA degradation.

OPPORTUNITIES IN SEAWATER USES: APPLICATIONS AND CIRCULAR ECONOMY

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In the energy transition scenario, green H_2 will play a central role, and, among several production processes, water electrolysis is recognized as one of the most promising technologies. However, looking at the hydrogen demand from the energy and transportation sectors, pure water availability could be considered a bottleneck for the 140 GW capacity, set by the EU. In the PROMETH2eus project, the use of seawater as raw material is foreseen and suitable application for residue brine has been investigated to find suitable applications and evaluate suitable strategies.

A detailed overview of seawater elements, excursion in terms of temperature and geographic locations, possible elements recovery, and available technologies have been considered, by deeply analyzing obtained salt mixtures and also the integration of brines coming from other sources, together with the integration of suitable industrial production processes like chlorine-NaOH production plants. In parallel, corrosion evaluation and sea water analysis have been investigated.

According to literature studies, several elements could be efficiently recovered, while other techno-economical aspects are the main limit, due to the quite low concentration.

As well, possible advanced applications of concentrated brine have been explored by our group, and the use of molten salts in chemical industries and plants has been targeted. At present, further exploitation is undergoing and they will be extensively discussed.

Among suitable applications, the use of molten salts as a reaction medium for some applications or even in the frame of catalyst production in relevant applications for energy transition scenarios, such as ammonia synthesis and decomposition, CO_2 utilization, upgrade of turquoise C-byproduct and use of graphite coming from exahust batteries can be considered, to develop advanced materials for energy transition and circular economy scenario.

CHARACTERIZATION AND COMPARISON OF VIRGIN AND RECYCLED POLYPROPYLENE FILAMENT FEEDSTOCKS FOR FUSED FILAMENT FABRICATION 3D PRINTING

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Polypropylene (PP) currently represents one of the most used commodity plastics for consumer goods, e.g., packaging and healthcare. Despite its use for long lasting applications, its properties are suitable for a wide range of single use disposable products, such as personal protective equipment. This fact leads to a significant amount of PP to be handled at their end of life, which can be reintroduced in new resource loops as a secondary raw material through alternative processes, e.g., additive manufacturing. This work compares the thermal, rheological, and mechanical properties of virgin and recycled PP filament feedstocks for Fused Filament Fabrication (FFF) and their printability for potential applications.

A commercial virgin PP filament and a 100% recycled one from the same manufacturer were selected for the tests. The filaments were 3D printed with a desktop size FFF 3D printer with a 0.4 mm diameter nozzle (Prusa i3 MK3S). The thermal and rheological characterization of the filaments before and after 3D printing was performed through Differential Scanning Calorimetry and flow stress ramp tests. The tensile properties were evaluated on two batches of 3D printed specimens following the ASTM D638-22 standard. Some 3D printed samples were fabricated to compare the printability of the two filaments.

Despite the additional thermomechanical degradation in extruding the recycled filaments, the 3D printed samples reached good overall quality in terms of extrudate consistency and shape retention, achieving similar results with virgin and recycled PP. No detachment, delamination or warping occurred during or, after the fabrication of the samples. The tensile tests also showed comparable values between the two filaments, confirming the limited impact of thermomechanical degradation on the 3D printed parts.

According to the tests, the recycled PP filament exhibits thermal, rheological, and mechanical properties comparable to the virgin feedstock. Its processability, dimensional stability, and achieved shape retention demonstrate the potential use of this recycled for 3D printing. These filaments can be used in different sectors, from furniture to assistive technology. Future work can consider products at their end of life as sources of recycled PP, e.g., disposable personal protective equipment, finding new ways to reintroduce them in new loops through 3D printing.

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A NOVEL MULTIFUNCTIONAL FINISH FOR THE ENHANCEMENT OF INDOOR AIR QUALITY: THE MAMMUT PROJECT

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Human activities are increasingly located in confined environments (e.g. homes, schools, offices, etc.), affecting in this way the comfort by VOCs, moulds, airborne particles, and inadequate relative humidity (RH) levels. This gives several effects on the health of occupants, including a disease caused by a poor-quality ventilation commonly known as Sick Building Syndrome.

The MAMMUT project explored the impact between an innovative multifunctional mortar and a commercial one on the Indoor Air Quality (IAQ). The commercial finish was used as a reference to test the following parameters: volatile organic compounds (VOCs), temperature (T), and RH which are fundamentals for the IAQ assessment. This study was conducted on a laboratory scale at first and then to a pilot scale. In both experimentations, the finishes were placed on the same type of commercial substrate.

The commercial finish used was Limepaint® which was applied on Calce Storica® as a substrate (both provided by Diasen Srl). This substrate was also employed for the innovative finish based on natural hydraulic lime, fly and bottom biomass ashes, and a unconventional adsorbent aggregates. The systems of substrate/finish were studied in terms of moisture buffering capacity (MBC), water vapor permeability (WVP), and depolluting activity (VOCs adsorption).

The system based on the innovative finish shows a better effectiveness on both laboratory and pilot scales. In laboratory, the depolluting activity was improved more than 200%, the MBC was enhanced by 100%, and WVP was increased by 15%. At pilot scale, the system based on innovative finish showed an increase of 25% in terms of MBC and a lower presence of indoors VOCs.

HYPOTHETICAL RESTORATION OF BUILDING HERITAGE OF 1900 USING SECONDARY RAW MATERIALS-DERIVED PORCELAIN STONEWARE TILES WITH SOLAR REFLECTIVE CHARACTERISTICS: A CASE STUDIO

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Sustainable construction focuses on reducing the environmental impact of buildings through (i) the design of construction materials following the principles of circular economy and (ii) reducing energy consumption. The first approach can be reached by modifying materials' formulations with secondary raw materials (SRM), i.e., wastes that replace conventional raw materials without affecting the properties of the product. Reductions in the energy consumption due to cooling in summer can be achieved by providing solar reflective (SR) characteristics to construction materials. SR is the ratio between the solar energy globally reflected by a surface and the total incident solar energy. Within sustainable construction, restoration of historic buildings is critical because it should ensure the structural and aesthetic integrity of the existing buildings to maintain their original appearance and technical characteristics but comply with the current requirements of energy savings. Here, we investigated the design of SRM-derived SR porcelain stoneware wall tiles with aesthetic, physical and optical characteristics suitable for their use in the hypothetical restoration of the Italian building heritage of 1900, particularly, former neighbourhood library (Biblioteca Pelagalli) building (Bologna, Italy) to increase its energy performance guaranteeing respect for the characterizing architectural/stylistic elements.

Tiles with SR property was prepared by incorporating four typologies of SRM in the engobe formulation, which was then used to prepare white and colored tiles through conventional pigments and an industrial production process. The aesthetic, thermal, optical, and physical characteristics of the engobe and tiles were evaluated. The urban planning and microclimatic and fluid dynamics analysis of the hypothetically restored building was carried out with the ENVImet software (state of affairs) during a day characterized by a heat wave.

Engobes with high SR were prepared using four typologies of SRM, but this property decreases when pigments are applied to prepare the colored tiles. From the analysis with ENVImet, the advantages and vulnerabilities present in the vicinity of the building under study before and after restoration with the SRM-derived SR porcelain stoneware wall tiles were obtained.

SRM-derived engobes can be used to develop SR colored and white wall tiles. However, as pigments partially cover the engobe, the SR of the colored tiles is limited. The analysis of the hypothetically restored building through ENVImet guarantees the possibility of intervention on the Italian building heritage to increase the energy, mitigation, and adaptation performance, while simultaneously respecting the architectural and stylistic language that distinguishes this heritage.

USE OF GEOPOLYMER-BASED MATERIALS CONTAINING PORCELAIN STONEWARE WASTE IN RESTORATION OF CULTURAL HERITAGE

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Porcelain stoneware represents the main type of production in the Italian ceramic industry, and it has been estimated that about 15 to 30% of this production is considered a by-product and/or waste generally intended for landfills. This contribution presents the preparation and characterization of new geopolymer-based mortars obtained from recycling waste deriving from the production process and the "end-of-life" of porcelain stoneware products. The excellent adhesion of these materials to common substrates such as pottery and earthenware, even for an elevated concentration of filler, suggests their use in the field of technical-artistic value-added applications, such as restoration, conservation, and/or rehabilitation of historic monuments, or simply as materials for building revetments.

Structural, morphological, and mechanical studies carried out on different kinds of mortars prepared by using several types of by-products (i.e., pressed burnt and extruded ceramic waste, raw pressed and gypsum resulting from exhausted moulds) point out that these systems can be easily cast, also in complex shapes, and show a more consistent microstructure with respect to the geopolymer paste, with a reduced amount of microcracks.

The materials developed in this work potentially offer the possibility of recovering and recycling up to 100% (almost endlessly) of not only waste materials and by-products of the ceramic industries (such as gypsum, raw pressed, and porcelain stoneware waste), but also the geopolymers themselves at the end of their use. In this way, a sensible reduction of the environmental impacts of these materials could be achieved and, in line with the Circular Economy approach, green and economically competitive products could be obtained.

The possibility of extending this approach to valorize and recycle ceramic wastes from different kinds of industries, together with in-depth structural and durability tests and studies on advanced modelling of the architectural composition, could open up new scenarios for making structural and functional elements for sustainable and advanced buildings.

HIGH-PERFORMANCE ARTIFICIAL LIGHTWEIGHT AGGREGATES BASED ON CEMENT, SILICA FUME AND MSWI FLY ASH

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In the modern construction sector, there has been a continuous pursuit for materials that are both lightweight and durable. This study aims to present an innovative technique for producing lightweight aggregates by combining cement, silica fume, and MSWI-FA, which are then shaped into spherical granules using a palletizer. The main goal of this synthesis process is to create lightweight aggregates with improved mechanical properties, making them suitable for a wide range of construction applications.

The experimental methodology carefully coordinates the exact mixing of cement, silica fume, and MSWI-FA in optimized proportions (10:10:80; 10:15:75; 15:15:70 respectively) to achieve the desired characteristics. The key component of the process is the use of a palletizer, which controls the granulation process to give the aggregates a unique spherical shape. This methodical approach not only guarantees consistency and uniformity in the physical characteristics of the aggregates, but also improves their structural strength. The assessment of mechanical properties involves conducting systematic experiments and analysis to comprehensively evaluate compressive strength, tensile strength, and durability.

The initial results indicate significant prospects, revealing significant enhancements in the mechanical properties of the lightweight aggregates compared to traditional counterparts. The addition of silica fume and MSWI-FA is a crucial strategy that greatly enhances the strength and durability of the aggregates. In addition, the granulation process highlights its effectiveness by giving the aggregates exceptional uniformity and compactness, thereby improving their overall structural resilience.

Using a spherical granule shape not only improves the physical aspect of the lightweight aggregates, but also increases their practical utility in various construction situations. This research has significant implications in the field of construction, providing a sustainable solution for the ongoing search for lightweight materials with exceptional mechanical properties. This methodology represents a significant change in construction practices towards environmental sustainability by utilizing the combined potential of cement, silica fume, and MSWI-FA. It promotes the development of sustainable infrastructure paradigms. Future research will focus on exploring the complexities of using lightweight aggregate in construction. The main goal is to drive significant advancements in modern construction methods.

FUNCTIONALIZED SILICA NPs FOR THE CONTROLLED RELEASE OF ANTIMICROBIALS TO PROTECT CULTURAL HERITAGE FROM BIODETERIORATION

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Heritage stone materials are subjected to degradation phenomena: biodegradation is considered one of the most dangerous factors which alter artworks' conservation state. Various methods to avoid it are employed, nevertheless, most of them are toxic and applied for cleaning interventions, hence with a time-limited action.

In this work, MCM-41 silica-based nanoparticles were employed as nanocontainer to hold and subsequently release the Biotin T antimicrobial product. Precisely, silica nanoparticles were grafted with sulphonic groups, aiming to modulate the release by modifying the silica matrix structure and its interaction with the antimicrobic active molecule.

MCM-41 was synthesized in a basic solution using TEOS and CTAB, and then removed through calcination. A post-grafting method was used to functionalize the material with –SH groups, employing MPTMS and NaCl, which were subsequently oxidated in –SO_3H with H_2O_2. The final material was labelled MCM-SO_3H. Impregnation was done with a Biotin T 30% aqueous solution. Microbiological tests were conducted to determine the product's antimicrobial activity. The nanomaterials were characterized by N_2 physisorption, XRD, TPO, TG/TDA, Raman and IR/ATR spectroscopy and SEM/TEM, whereas the Biotin T release was studied through UV spectroscopy.

Microbiological tests demonstrated that the biocide is effective even at low concentrations, therefore antimicrobial actions can be easily achieved. The successful functionalization was asserted by TPO, TG/DTA, Raman and IR/ATR spectroscopy, showing characteristic signals of sulfonic groups. XRD, N_2 physisorption and SEM/TEM analyses underlined a more heterogeneous pore sizes distribution in MCM-SO_3H: the grafting treatment modified the matrix structure also showing a loss of the original short-range order. In comparison to MCM-41, MCM-SO_3H was able to gradually deliver the active molecule with a release of ~50% after 30 days.

The multifunctional functionalized silica nanoparticle-based matrix can encapsulate and gradually release the commercial biocidal product, Biotin T. The matrices MCM-41 and MCM-SO_3H did not only differ chemically: after functionalization, the porous structure was slightly modified leading to a higher interaction with the antimicrobial product. MCM-SO_3H less ordered porous structure favors the release of a greater quantity of biocide compared to MCM-41.

PRESERVING ART: SCIENTIFIC IN-DEPTH STUDY ON THE DEGRADATION OF CADMIUM PIGMENTS

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The crucial importance of developing scientifically grounded approaches to understand and mitigate the degradation of artistic materials lies in providing essential tools and methodologies for the conservation and restoration of cultural heritage. The pursuit of effective techniques assumes a central role in ensuring the long-term preservation of artistic heritage.

During this study, a thorough examination of the degradation of cadmium pigments, when mixed with oil and applied to canvas, was conducted. The primary objective was to investigate the degradation process of the isolated pigment, considering the crucial role that the canvas and binder (oil) can play in altering the colorimetric properties of the final painting.

The artificial simulation of degradation was achieved through the irradiation of samples using UVA (365 nm) and UVC (250 nm) light sources. The optical characterization of the material was performed employing advanced techniques, including pump-probe spectroscopy, Raman spectroscopy, and colorimetric analysis.

While pure pigments do undergo reactions with the environment, resulting in the formation of a surface patina of oxides and sulfates, it has been revealed that initially, the oil acts as a protective layer, inhibiting this process. However, both the oil and the canvas experience harmful effects from exposure to UV rays, leading to alterations characterized by darkening and yellowing. Under these conditions, a reduction in the protective effect has been observed, leaving the pigment vulnerable to atmospheric agents.

These results not only enrich our understanding of the degradation mechanisms present in artistic paintings but also unequivocally highlight the dynamic interplay among the different fundamental components: the pigment, the oil, and the canvas. Such profound understanding holds crucial importance for the field of art conservation and restoration.

The detailed analysis of interactions between pigment, oil, and canvas provides a more comprehensive and nuanced picture of the complex artistic deterioration process. The phases and dynamics involved become clear, thereby contributing to the development of more targeted and effective strategies for the long-term preservation of artistic heritage.

It is noteworthy that the approach used in this study relies on advanced, non-destructive techniques. This represents a significant advancement in art research, allowing for detailed information to be obtained without compromising the integrity of the original material.

ON-SITE PERFORMANCES OF A NEW NANOLIME, OBTAINED BY A SUSTAINABLE AND LARGE-SCALE PROCESS, FOR CONSERVATIVE TREATMENTS OF HISTORIC, ARTISTIC AND ARCHITECTONIC SURFACES

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Recent advances in nanotechnology have enabled fabrication of therapeutic and/or diagnostic nanocarriers with high efficacy for treatment of several pathologies, such as cancer and neurological diseases. For clinical purposes, artificial nanocarriers with tailored properties and functionalities can be produced in laboratory and composed of organic and/or inorganic components. Lipid-based nanocarriers (e.g. micelles, liposomes, solid lipid nanoparticles), as well as polymeric nanoparticles, represent the most commonly organic nanostructures explored for biomedical applications, being able to incorporate drugs or imaging agents and target them to the specific disease sites. Along with the lab-developed nanocarriers, natural vesicles, physiologically emitted from plant and animal cells and actively involved in the intercellular communication, such as exosomes and extracellular nanovesicles, can be used as delivery systems of therapeutic and /or diagnostic agents, offering several advantages respect to the artificial nanocarriers, such as higher stainability, safety, biocompatibility and bioavailability, biorecognition and targeting ability.

Nanostructures, based on metals, semiconductor, carbon, silica or oxide-based nanomaterials are combined to lipid-based, polymeric and silica based nanocarriers in order to obtain hybrid nanoplatforms with unprecendented targeting, drug delivery ability, as well as photoactivity and/or magnetic properties, all relevant in the clinical field. Extracellular vesicles samples are also isolated and characterized.

Here, design, preparation and characterization of different multifunctional synthetic nanovectors along isolation and characterization of physiologically emitted natural vesicles are presented for the diagnosis and therapy of specific diseases, as cancer (e.g. gastrointestinal cancers) and neurological disorders. In particular, mesoporous silica nanoparticles, lipid or polymer based nanocarriers obtained by using selected preparative approaches is described. Also, the integration in such nanocarriers of luminescent, magnetic and photoactive inorganic colloidal nanoparticles is performed, in order to achieve multifunctional nanovectors fabrication. The physical chemical investigation and the biological viability of the application of the prepared nanovectors has been accomplished. The extra cellular vesicles isolation and characterization are also carried out.

The potential for incorporation in the prepared nanovectors of drugs and/or inorganic nanoparticles and for the surface functionalization of the prepared systems to achieve novel drug delivery targeted nanoformulations with elevated colloidal stability, stealth properties, good degrees of biocompatibility and high encapsulation efficiency is discussed. Finally, The relevance of natural cell-derived exosomes for diagnostic of gastrointestinal cancer is considered.

VALORIZATION PATHWAY FOR METALLURGICAL BY-PRODUCTS OF THE PORTOVESME S.R.L. PLANT IN CEMENT-BASED MATERIALS FORMULATION: MECHANICAL, TECHNOLOGICAL BEHAVIOUR AND ENVIRONMENTAL ANALYSIS

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Cement is one of the most used materials in the global civil engineering industry. However, the cement manufacturing consumes approximately 12-15% of total industrial energy use and causes about 5-8% of the global man-made emission of CO_2. The current efforts regarding this crucial environmental challenge are focused on reducing the cement-to-binder ratio by the implementation of alternative materials and wastes as partial replacement of conventional cement powder. The future availability of industrial by-products commonly used as supplementary cementitious materials (fly ash or granulated blast furnace slag) does not match the worldwide demand for concrete production. As a result, the research on alternates sources of cementitious materials remains an active area of investigation towards eco-friendly approaches in the construction industry. Waelz slag (WS), an iron-containing waste fraction generated during electric arc furnace dust processing, was explored in this study as a novel and sustainable feedstock to be used as a replacement for cement powder to develop cement-based mortars. WS were kindly supplied by Portovesme Srl. Glencore metallurgical plant (Portoscuso Cagliari, Italy). As-received ground slag was first screened to obtain a grain size suitable for blending into the cement mixtures. In addition to the chemical, physical and microstructural characterization, the pozzolanic reactivity analysis on WS was implemented to select proper substitution ratios with cement powder. Then, mortars with different WS-cement replacement levels (0%, 5%, 10% and 20% by weight) were produced and characterized in terms of rheology, mechanical properties, permeability, thermal stability, and microstructure. An LCA model was developed to determine the environmental impact of the cementitious mixtures following the incorporation of WS. Then, a sustainability index (M-EASI), covering both the engineering and environmental performance of the investigated formulations, was proposed to determine the optimal content of WS.

The study revealed that WS can be used as interesting cementing additive into a percentage of 5% and 10% without compromising the technological properties of the material while inducing benefits in ecological terms. Indeed, the mixtures adding with 5% of WS displayed a slight improvement in mechanical strength compared to the control sample. The presence of sulphur in the slag enabled the formation of primary ettringite, which increased the packing and strength of the material. However, the highest amounts of WS hindered the workability and correct hydration of the cementitious mixture, limiting the further improvement in strength and microstructure of the hardened mortars.WS are valuable resources for achieving performing and sustainable materials, enabling the transition towards greener built environment. The implementation of sulphur-containing powder must be carefully analysed due the high-sensitivity of cement-based materials on ettringite formation. More detailed studies will be necessary to refine the mix designs in agreement with the preliminary results achieved.

SOL-GEL SYNTHESIS OF NANOSTRUCTURED MATERIALS FOR QUANTUM SOURCES

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The development of nanostructured nonlinear optical (NLO) materials play an increasingly key role in photonics, due to their advanced functionalities. NLO processes in solid-state materials are widely used for generating quantum light, including single photons, entangled-photon pairs, and quadrature-squeezed states. Nanostructured materials whose NLO response can be finely tuned by the chemical composition and suitable heat treatments can be obtained by sol-gel routes inspired to sustainability and circularity criteria of Green Chemistry.

Sol-gel nanomaterials belonging to Nb_2O_5-SiO_2 system, with variable contents of high polarizable element were obtained. To obtain film/gel-derived materials with amorphous and/or crystalline nanostructuring proper drying and heat treatment programs were explored.

A chloride-free sol-gel route, starting from tetraethoxysilane, $Si(OC_2H_5)_4$, and ammonium niobium oxalate hydrate, $NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot nH_2O$, to obtain transparent chemical gel was established. Different compositions were obtained with a Nb_2O_5 content ranging from 2.5 to 20 mol% without the use of mineral acids. The gels were fully dried in air at 110 °C in an electric oven. The hardened dry gels were finely ground to allow the thermal and structural characterization. Namely, nanostructured samples were obtained by thermal heat-treatments in air between 400 – 800°C.

The choice of ammonium niobium oxalate hydrate as Nb precursor allows the safety aspects and chemical requirements of the synthesis to be combined. It is easily handled in air, soluble in water and does not cause precipitation of hydrated niobium pentoxide, owing to the chelating effect of oxalate ligands. To avoid the use of any organic solvent the hydrolysis of the precursors was performed only using water. No mineral acid catalysts were required because of the acid catalytic function of Nb precursor in the initial solution.

The structural evolution with the temperature of the synthesized gels showed the formation of amorphous and or crystalline nanostructured samples according to the Nb content.

Ag NANOPARTICLES DECORATED REDUCED GRAPHENE OXIDE - SYNTHESIS AND EVALUATION OF LONG-TERM ANTIMICROBIAL ACTIVITY OF THE NOVEL HYBRID NANOCOMPOSITE AS A TEXTILE COATING

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In response to the significant demand for effective pathogenic bacteria control and the limitations of traditional treatments, the advancement of antimicrobial materials has become imperative. Ag nanoparticles (NPs) are among the most widely used solutions for tackling this issue due to their broad biocide effect, however their strong tendency to aggregate and oxidase, leads to a remarkable deterioration of their antibacterial activity. Reduced Graphene Oxide (RGO) has been found an ideal scaffold for stabilizing Ag NPs and their biocidal effect.

A novel, in situ, colloidal approach was used for synthesizing a new colloidal hybrid nanocomposite formed of RGO functionalized with histidine (His), and decorated with citrate coated Ag NPs, starting from AgNO3 in presence of trisodium citrate and sodium borohydride. The role of the synthetic parameters on the morphology of the Ag NPs and on their coating density onto His-RGO, has been investigated to elucidate the mechanism of the NPs formation. The quantitative standard ISO 20743:2021 protocol was used to assess the hybrid nanocomposite as an antimicrobial coating against E. coli upon transfer on cotton, against coatings based on His-RGO and Ag NPs.

The results demonstrated that (i) His anchors the Ag NPs onto RGO by coordination to its -COO- and -NH_2 groups, (ii) borohydride accomplishes reduction of AgNO3 to Ag NPs and controls their morphology at the early stages of the growth, and (iii) citrate behaves as a strong coordinating ligand dictating the final morphology of the NPs. Ag NPs, 24±4 nm in size, were found to form onto His-RGO by an aggregative growth process, and the interplay between trisodium citrate and borohydride concentration, along with the pH, were found to define sheets coating density, as well as NPs morphology. The nanocomposite showed a superior and longer-term biocidal effect with respect to neat Ag NPs based coatings.

The nanocomposite biocidal impact stems from the release of Ag^+ ions by the Ag NPs and ROS generation. Its sustained antimicrobial efficacy over time is attributed to His-RGO ability to prevent NP aggregation and shield them from oxidation, thanks to its gas and moisture barrier properties.

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PLASMA-ASSISTED GROWTH OF CARBON NANOTUBES ON CONTINUOUS FIBERS AS REINFORCING AGENTS IN MULTIFUNCTIONAL POLYMER COMPOSITES

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Poor fiber/matrix interfacial adhesion is a critical issue in fiber-reinforced polymer (FRP) composites, prompting exploration of various techniques. Surface integration of carbon nanotubes (CNTs) emerges as a promising solution thanks to the hierarchical reinforcement structure providing, in addition, inherent multifunctionality. Thermal chemical vapor deposition (T-CVD) is notable for its ability to tune the orientation of high-density carbon nanostructures. However, the high-temperature environment adopted can degrade the fiber tensile properties. To address this concern, plasma-enhanced (PE)-CVD technology is proposed, utilizing a high-energy plasma to supply energy for hydrocarbon decomposition and CNT formation.

An iron-based catalyst precursor was deposited onto quartz fibers through dip-coating. A high vacuum reaction chamber equipped with an RF-plasma module and a gas-shower cathode was utilized for CNT growth where 4-minute annealing treatment in H2 atmosphere and 10-minute growth in acetylene flow were conducted. In the PE-CVD process, the growth step was carried out with a plasma power of 30 W.

This study focuses on the growth of CNTs on quartz fibers through T-CVD and PE-CVD. A comprehensive morphological investigation is conducted, and the multifunctional properties are highlighted through electrochemical analyses. Traditional T-CVD process at temperatures of 620-640 °C led to the growth of densely-packed arrays of vertically-aligned CNTs organized in a Mohawk-like morphology. In contrast, the PECVD process allowed for lower operating temperatures (520-540 °C), producing radially-aligned CNTs.

The different CNT morphologies are compared in terms of CNT length, orientation, and spatial arrangement. The distinctive curly morphology observed after T-CVD is absent when PECVD is employed, as the electric field during the process promotes the development of more straight and aligned structures. Electrochemical tests demonstrate that these carbon-based materials exhibit electrical reactivity, showcasing promise for applications in supercapacitors.

FABRICATION OF HIGH ENTROPY DIBORIDE - SiC COMPOSITES THROUGH SELF PROPAGATING HIGH TEMPERATURE SYNTHESIS AND SPARK PLASMA SINTERING

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High entropy borides (HEBs) are a new type of Ultra-High Temperature Ceramics that combines four to five constituents in nearly equimolar ratios to form single phase crystalline solid solutions with high configurational entropy. Some HEBs have been shown to exhibit superior oxidation resistance and mechanical properties compared to their individual constituents, making them highly attractive for high-temperature applications. Due to their refractory nature, the fabrication of additive-free HEBs can be challenging. In addition, they generally possess scarse oxidation resistance at high temperatures and low fracture toughness. These limitations can be overcome using advanced synthesis/sintering technologies and/or inserting secondary Si-containing phases. This work successfully adopts a two-step process that combines Self-Propagating High-Temperature Synthesis (SHS) with Spark Plasma Sintering (SPS) to prepare $(Hf_{0.2}Mo_{0.2}Ti_{0.2}Ta_{0.2}Nb(or\ Zr)_{0.2})B_2$-SiC.

The precursors (transition metal powders, B_4C, and Si) were first reacted through SHS and then sintered via SPS under vacuum. Sintering conditions were optimized by varying the dwell temperature (TD) and holding time in the ranges 1500-1900°C, and 5-20 min, respecively, whereas heating rate (200°C/min) and applied pressure (20 MPa) were kept constant. The densification behaviour of SHS powders, microstructure, mechanical properties, and oxidation resistance of the sintered products were evaluated and compared with those of SiC-free counterparts.

The precursors underwent partial conversion via SHS, but the completion of the synthesis was achieved by SPS under optimised conditions (1800°C, 20 min). The resulting samples displayed a uniform microstructure, relative densities above 97% and improved mechanical properties, compared with SiC-free products. Additionally, $(Hf_{0.2}Mo_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})B_2$-SiC, exhibited superior fracture toughness (7.35 MPa $m^{1/2}$) with respect to $(Hf_{0.2}Mo_{0.2}Ti_{0.2}Ta_{0.2}Zr_{0.2})B_2$-SiC. (4.11 MPa $m^{1/2}$). Samples containing SiC also showed better oxidation behaviour at high temperature. The addition of SiC has been found to be highly beneficial for improving the sintering behaviour, mechanical strength, and oxidation resistance properties of both HEBs. The in-situ synthesis of HEB and SiC phases during the SHS-SPS process promotes the establishment of strong interfaces between them, thus enhancing the performance of the resulting material. The introduction of SiC led to a significant improvement in the KIC value due toughening mechanism, such as crack deflection and branching. SiC also plays a key role in protecting the ceramics from the volatilization of metal oxides formed during oxidation tests.

RAPID FIRING OF 3YSZ: ON THE HEATING RATE IMPACT ON SINTERIN, PROPERTIES AND MICROSTRUCTURE

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Yttria-stabilized zirconia (YSZ) finds several applications as a structural material operating at high temperatures in harsh environments and in the field of energy storage and conversion. Its sintering is challenging and requires high temperatures, generally exceeding 1400°C.
Ultrafast high-temperature sintering (UHS) is currently emerging as a powerful tool to consolidate ceramics in the seconds/few minutes timescale. It employs graphite felts as resistive heating elements that, due to the low thermal capacity, can be heated to ultrahigh temperatures in a matter of seconds.
Herein, we study the UHS of 3YSZ nanopowders with different particle sizes in Ar and N_2 atmosphere. The densification is studied as a function of the sintering conditions and compared with the density expected from low heating rate sintering experiments. The samples are characterized from a structural (XRD, Raman), microstructural (density measurements, SEM, TEM, Hg porosimetry), mechanical (hardness), and electrochemical point of view (EIS).
The results show that effective densification can be attained in a very short time scale and at temperatures significantly lower than that required for conventional sintering. Such an effect is attributed to the microstructural refinement induced by rapid heating when treating nanograined YSZ powders (particle size about 20nm). On the other hand, the heating rate impact on densification is reduced when considering green bodies obtained with coarser powders. In this case, analytical models extrapolated during conventional heating can be used to predict the densification also under extreme heating rates.
When UHS is carried out in N_2, nitrogen ions are incorporated into the YSZ lattice leading to peculiar phase evolution. Materials with mechanical properties similar to conventional sintering are obtained, on the other hand, UHS allows rapid manufacturing of excellent ionic conductors. The results pave the way to rapid processing of 3YSZ components with electrochemical properties superior to those of conventionally sintered materials. The reduction of the processing temperature and time promises a huge advantage in terms of productivity and carbon footprint reduction. Rapid sintering allows a fine-tuning of the final structure and microstructure going beyond the existing literature and current industrial practice.

LEAD HALIDE PEROVSKITES AS SENSITIVE MATERIALS FOR SOFT X-RAY RADIATION DETECTION IN SPACE ENVIRONMENTS

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Lead halide perovskites have garnered significant attention within the scientific community due to their potential as absorber materials for solar cells, showing promising results. However, beyond their photovoltaic applications, lead halide perovskites exhibit intriguing properties that can be harnessed for various devices. With their high stopping power, defect tolerance, large mobility-lifetime product, and high sensitivity per unit volume, lead halide perovskites have recently emerged as promising candidates for photodetectors. This research, funded within the PE15 project "Spaceit Up!" aims to develop a radiation sensor capable of detecting soft X-ray radiation intensity in space environments.

For this study, $CsPbCl_3$ was chosen as the active material for sensor fabrication due to its relatively high bandgap (3.0 eV), in the range of UV light. Various deposition methods exist for fabricating perovskite thin films, ranging from wet methods involving the dissolution of precursor salts in solvents to solvent-free approaches. We employed a physical vapor deposition (PVD) method via a magnetron sputtering source powered by an RF working mode power supply to hit a target composed of equal molar ratios of the precursor salts: CsBr and $PbBr_2$. Subsequently, the recondensed vapor on the substrate yielded smooth and uniform thin films of $CsPbCl_3$ perovskite.

The deposited thin films underwent comprehensive characterization. Scanning electron microscopy (SEM) assessed the film uniformity and morphology, X-ray photoelectron spectroscopy (XPS) confirmed the expected chemical composition while the formation of the crystal structure was verified by X-ray diffraction (XRD).

PVD deposition of multi-element materials like perovskites can lead to films with stoichiometric variations compared to the target due to different sputtering yields of constituent elements. This challenge can be addressed by adjusting the target composition to enrich the element with the lower sputtering yield. In our study, XPS measurements validated the correct composition of the fabricated films. XRD analysis indicated the presence of the perovskite crystal structure, albeit with high texture, a typical characteristic of films deposited via PVD methods. Furthermore, SEM imaging revealed uniform and continuous film coverage across the deposition substrate.

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PROCESSING AND CHARACTERIZATION OF DENSE $(Zr_{0.5}Ta_{0.5})B_2$ AND $(Zr_{0.5}\,Hf_{0.5})B_2$ ULTRA HIGH TEMPERATURE CERAMICS

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The combination of their unique chemical and physical properties makes Ultra-High Temperature Ceramics based on transition metal diborides very attractive for various high-temperature applications. In this context, while individual diborides (HfB_2, ZrB_2, etc.) have been widely investigated in literature, binary metal diborides have been barely explored.

In this work, the fabrication of nearly full dense $(Zr_{0.5}\,Hf_{0.5})B_2$ and $(Zr_{0.5}Ta_{0.5})B_2$ solid solutions is performed by combining Self-Propagating High Temperature Synthesis (SHS) and Spark Plasma Sintering (SPS). The effect produced by the introduction of small amounts of graphite to the SHS powders prior to SPS is examined. The optimal sintered products are characterized from the mechanical and oxidation viewpoints.

Zr, Hf (or Ta), and B precursors are first reacted in stoichiometric ratio by SHS, and the resulting powders then processed, without or in presence of graphite via SPS under vacuum. The densification behaviour of SHS powders, as well as the composition, microstructure, mechanical properties, and oxidation resistance (in stagnant and flowing air) of SPS products are evaluated.

Initial reactants were not fully converted by SHS into the desired binary phases. The latter goal could be reached during the subsequent SPS process conducted at 1950°C/20min, but, when graphite free powders were used, samples were rich of oxide impurities and showed scarce relative densities (87-90%). In contrast, highly dense (97.5-98%) and purer boride solid solutions were produced at a lower temperature (1850°C) when adding 1 wt.% graphite prior to sintering. It is important to note that the $(Zr_{0.5}Ta_{0.5})B_2$ solid solution is obtained for the first time in literature, as a single boride phase.

Superior mechanical properties were shown by the binary ceramics with respect to ZrB_2. Moreover, mechanical performances of $(Zr_{0.5}Ta_{0.5})B_2$ were better than $(Zr_{0.5}\,Hf_{0.5})B_2$, whereas the latter system exhibited higher oxidation resistance at elevated temperatures.

The results obtained in this work evidence that coupling the SHS and SPS methods provides a powerful tool for the fabrication of dense binary refractory diborides like $(Zr_{0.5}Ta_{0.5})B_2$ and $(Zr_{0.5}\,Hf_{0.5})B_2$. In addition to the efficient synthesis and sintering techniques used to this aim, a prominent role is played by graphite, to reduce oxide impurities by carbothermal reaction, improve powder densification, and make the required temperature milder. The Ta-containing system displays better mechanical properties, while $(Zr_{0.5}\,Hf_{0.5})B_2$ shows superior oxidation resistance. Both systems can be considered very promising base candidates for high temperature applications.

INTEGRATING HIGH-SPEED NANOINDENTATION AND MACHINE LEARNING: A NEW PARADIGM FOR ADVANCED STEEL DESIGN AND QUALITY ASSESSMENT

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Integrating High-Speed Nanoindentation Mapping (HSNM), EBSD, and machine learning revolutionizes AHSS analysis, crucial for ICT, Energy, and Space industries. This methodology enhances phase identification, optimizes material design, and supports the circular economy by improving sustainability and efficiency in material use. Specifically, TRIP steels suffer from proper identification of Bainite and Ferrite phases. The new mechanical microscopy approach overcomes the frequent limitations of SEM-EBSD standard analysis in distinguishing between phases with identical crystal structures (BCC, FCC, etc.).

This study integrates HSNM with EBSD analysis, leveraging sophisticated machine learning algorithms to create a robust structure-property relationship at the nanoscale. The methodology begins with machine learning-informed HSNM, utilizing the expectation-maximization algorithm to fit probability distributions of nanoindentation data for deriving primary mechanical phase statistics. This allows for the correlation of elastic modulus and hardness with specific microstructures using nanoindentation data alone. The process is refined through a supervised machine learning approach, ensuring precise EBSD and nanoindentation data mapping through advanced image analysis and data clustering techniques. The application of machine learning extends to analyzing Inverse Polar Figure (IPF) mapping for understanding grain anisotropy and characteristics, with k-nearest-neighbors regression employed for data imputation to address gaps in descriptors related to nanoindentation, grain boundaries, and EBSD phases.

The integration of HSNM with EBSD and ML algorithms enabled precise identification and quantification of complex phases in advanced high-strength steels (AHSS). Notably, this methodology facilitated the detailed analysis of bainite, ferrite, and martensite phases. Key numerical findings include:

- Bainite was characterized by an elastic modulus of 214 GPa and hardness of 8.03 GPa.
- Ferrite showed an elastic modulus of 213 GPa and hardness of 6.61 GPa.
- Martensite displayed an elastic modulus of 195 GPa and a higher hardness of 9.51 GPa.

This approach provides distinguishable and precise data for Bainite and Ferrite for the first time. The modular strategy is adaptable for similar or multiple output correlations within the same ROI. However, biases may arise from imprecise pixel comparison, image quality, and dataset size, affecting accuracy and statistical representation. Despite limitations in existing characterization techniques and data variability, this study proposes a data-informed approach, leveraging computational intelligence to assess steel structures and properties more objectively, addressing knowledge gaps and advancing materials science. The methodology's applicability extends to composite materials, cement, industrial coatings, 3D-printed metals, and natural materials, indicating its potential for broad adoption.

MICROPLASTICS POLLUTION: MAIN SOURCES AND THE ROLE OF THE PLASTICS INDUSTRY

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Nowadays, the exponentially increasing utilization of plastics has been posing downsides and threats in terms of environmental impacts Due to unsatisfactory recycling procedures and rates, and the wellknown lack of biodegradability of traditional plastics, the persistence of plastic-based items can lead to the formation of microplastics (size < 5 mm) with multiple and concerning environmental impacts, affecting soils, fresh and marine waters, air. Furthermore, even more dangerous particles of smaller size, i.e. nanoplastics, can be formed. Microplastics (and, in turn, nanoplastics) typically come from a combination of two primary pathways, i.e. direct and/or unintended release into the environment, and the multiple degradation phenomena that can affect larger plastic items (macroplastics) but also from products such as paints, tires and textiles during their life cycle. It is estimated that, by 2060, global plastic leakage into the environment should double to approx. 45 million tonnes/year with subsequent accumulation of plastics into water bodies estimated to triple. In general, it can be stated that microplastics have been found in all the water ecosystems as well as in food and drinking water, and their continuous release leads to several concerns since exposure to microplastics has been linked to a series of negative ecotoxic and physical effects on living organisms. There are, in summary, several mechanisms and sources involved, which in turn require accurate classifications and complicate the full understanding of the problems linked to the environmental release of these levels of pollutants, and the development of adequate strategies for containment.

In this work, we performed a Literature review aimed at providing a synthetic overview of the main aspectsregarding the sources of microplastics and nanoplastics release into the environment, their nature, some of the consequences for the marine environment.

The review of multiple literature sources pointed out that, differently from the public opinion's perception and despite the allegations from some think-tanks or environmental protection groups, there is not sufficient evidence that microplastics and, even more, nanoplastics pollution is significantly affected by the commercial use of polymer packaging, while much more significant sources are paints, tires, and textiles.

DEVELOPMENT OF A PP-BASED MATERIAL WITH FLAME RETARDANT PROPERTIES FOR 3D PRINTING

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Fused filament fabrication (FFF) is one of the most used techniques for 3D printing of thermoplastic materials. Despite the rapid development of FFF techniques, their application is still limited by the modest availability of suitable materials. In particular the use of polypropylene (PP), one of the most studied and used polymer, is still very limited and challenging in FFF process. In addition, there is a lack of functionalized PP-based materials, including, for example, those with flame-retardant properties. In this context, a PP-based flame retardant filament suitable for FFF processing and its burning behavior were developed.
A polypropylene-polyethylene random copolymer (PP COPO), the organophilic phyllosilicate Cloisite 20A (C20A) and polypropylene-graft-maleic anhydride (PP-g-MA) were used. The nanocomposite PP COPO + 5% C20A + 3% PP-g-MA was produced through melt compounding in a twin-screw extruder. After that a filament suitable for 3D printing was successfully prepared and samples for cone calorimeter test were produced by FFF process. In order to make a comparison, the same specimens were also produced by compression molding. A complete thermal, rheological, and morphological characterization was performed on the materials obtained.
First, it was verified that the nanocomposite had the rheological characteristics suitable for the 3D FFF process with in particular the presence of the yeld stress behavior at low frequencies.
After that, the process conditions to obtain the filament were optimized with special attention to the cooling parameters of the wire exiting the extruder to avoid ovalization of the filament. After that, samples were produced and tested for flame-resistant properties.
At the cone calorimeter, an improvement in behavior was found with a lowering of the peak HRR by 30 percent. Also comparing the carbon residues obtained from the FFF process and compression molding, it was noted that the former gave better compactness of the protective layer of the polymer giving promising results. Finally in the UL-94 test, it could be found that again with the FFF process, comparable or better results were obtained than the compression molding process but also with the different effect of the methodology of deposition of the filament to go to form the specimen.

3D PRINTING OF PHOTOCURABLE ELASTOMERIC COMPOUNDS

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The possibility of 3D printing elastomers materials is of enormous interest since they find very wide applications in industrial fields such as automotive and aerospace. Until now, Additive Manufacturing (AM) technologies have not been applied to this type of materials due to the vulcanization issues which is not compatible with the AM technologies currently on the market. In this work, a novel 3Dprinting method, with a two-steps crosslink system (UV and thermal crosslinking), has been developed to successfully process liquid elastomeric compounds filled with nano- and micrometric fillers.

Different formulations of butadiene rubber-based compounds suitable for UV cross-linking using thiolene chemistry and peroxide vulcanization have been prepared, adding several carbonaceous and silica fillers (i.e. carbon nanotubes, carbon fibres and silica). The produced resins have been 3D printed with a modified commercial FFF printer, able to process high viscosity materials and UV cured after each layer deposition. 3D printed samples have been further thermally cross linked (peroxide vulcanization) to a hydrostatic vulcanization system (5 Bar, 160 °C). The elastomeric compounds and 3D printed samples have been characterized in terms of mechanical and rheological properties. The cross-linking reaction was studied using infrared spectroscopy, FT-IR.

The rheology curves of carbonaceous and silica reinforced compounds show a shear thinning behaviour with viscosities ranging from 50 to 240 Ps. FT-IR analyses show the variation in intensity of the peaks related to the absorption band of the bonds involved in the cross-linking process. Cured samples show elongations at break greater than 200%, ultimate tensile stress ranging from 0.2 to 0.8 MPa, shore A hardness between 30-40 and high dumping behaviour ($\tan\delta > 1$).

The viscosity of compounds and is highly influenced by the nature, content, dimension and dispersion of the fillers. FT-IR analysis confirm the success of the two-steps cross-linking process. As the filler content increases the ultimate tensile stress increases and the elongation decreases. The samples show excellent low frequency damping values. In conclusion, elastomeric compounds have been successfully 3D printed with a suitable system and the produced resins can be used for the rapid prototyping of elastomeric industrial components.

HARNESSING POLYETHYLENEIMINE IN 3D PRINTING FOR TUNABLE HETEROGENEOUS CATALYSTS

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Polyethyleneimine (PEI) is a family of polymers with interesting properties, mainly due to the presence of nucleophilic nitrogen atoms, that lead to their use in different fields, from gene delivery and drug release devices to environmental remediation tools and catalysis. In most cases, PEI is used as a grafting agent or as a support for catalytically active metals, whereas only few cases report its use in amine-catalysed organic transformations. The main drawbacks concern PEI's high viscous liquid state, complicated to dose, and its good solubility in lots of solvents, with a subsequent difficulty in separating PEI from the reaction mixture. Hence the idea of using modified PEI as innovative material in a 3D printing process to craft a tuneable in-flow reactor able to work as a heterogeneous catalyst.

Branched polyethyleneimine (b-PEI) and polyethylene glycol (PEG) at different MW were reacted with methacrylic anhydride, obtaining polymers with various grafting degrees. Cylindric samples with different porosity were produced via photopolymerization during the printing process by using a Digital Light Processing (DLP) 3D-printer. Lithium phenyl-2,4,6-trimethylbenzoylphosphinate was added as a photoinitiator, and tartrazine was used as a photo-absorber. Divinylbenzene served as a crosslinking agent. Materials exhibiting optimal printing accuracy were characterized using SEM microscopy and subjected to mechanical testing.

The first part of the study was focused on finding the appropriate grafting degree of b-PEI with methacrylic anhydride to obtain scaffolds with proper mechanical properties and stability. A printability screening of pure materials and different blends has been carried out by designing cylinders with different porosity. The mechanical properties of the printed scaffolds were tuned by blending divinylbenzene as hardener, PEG as plasticizer, and by varying the chain length of both polymers.

The feasibility of printing b-PEI-based materials with catalytic potential was demonstrated, as evidenced by successful applications in Gewald, Knövenagel, and Suzuki-Miyaura coupling reactions. Leveraging the flexibility and reproducibility of 3D printing, this method lays the groundwork for crafting a customizable in-flow reactor for heterogeneous catalysis. The scalability of this technology renders it attractive for future industrial development.

POLYMER NANOCOMPOSITES AS INNOVATIVE ENCODING/DECODING MAGNETIC TAGS

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The exchange of data and information via internet connection requires the development of highly efficient and advanced cybersecurity strategies to counter cyber-attacks and counterfeiting attempts in defense of the world economy, national security, and human intellectual property. A controlled assembly of magnetic polymeric supraparticles (MPSs) can represents an innovative magnetic tag in the encoding/decoding technology able to exchange, track, identify, and encrypt information.

MPSs were prepared using an oil-in-water emulsion solvent evaporation method: polymer pellets were dissolved in chloroform ($CHCl_3$)/magnetite nanoparticles (Fe_3O_4) dispersion and then added dropwise to an aqueous solution of poly(vinyl alcohol). Different polymer matrices and Fe3O4 concentrations were tested. The emulsion was kept under mechanical stirring at room temperature until $CHCl_3$ evaporation. The resulting MPSs were washed with water and oven-dried at 40°C. The powder was then collected and sieved at 150 μm.

Microscopic characterisation of MPSs shows a regular spherical particle geometry and laser particle size confirms a size distribution centred around 50 microns, consistent with the sieve size. The hysteresis loops at room temperature exhibit a hysteretic behaviour with a coercive field of approximately 90 Oe for both Fe_3O_4 and MPSs. The saturation magnetization in emu/g is lower in MPSs, proportionally related to the Fe_3O_4 concentration in the polymer shell selected during the preparation phase.

By normalising the magnetic signal with the saturation magnetisation value, we can observe the magnetization curves of Fe_3O_4 and MPSs perfectly superimposed. This confirms that the confinement of the polymer shell has no effect on the magnetic properties of the Fe_3O_4. This magnetic fingerprint has the potential to enhance research in the field of encoding/decoding using nanomaterials. It possesses crucial characteristics such as high stability over time, resistance to adverse environmental conditions, remote decoding, and easily expandable coding capacity.

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CONTROLLING THE CONFORMATION OF REDISSOLVED SILK FIBROIN FOR PRINTABLE MULTIFUNCTIONAL 3D MATERIALS

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Printable proteins offer a broad range of applications including biointerfaces, optics, and biodevices. Here, we present a study that mimics natural silk spinning, wherein fibroin, present initially in a silk I-like conformation, is converted into silk II, which is largely formed from crystalline β-sheets, as fibroin passes from the posterior to the anterior division of the silkworm glands. The conformational transition of silk fibroin (SF) is enabled by the modulation of SF concentration, pH, sonication time or metal-ion content. Thanks to this holistic approach a number of 3D multifunctional materials for various applications are shown. These applications range from shape-morphing hybrid biomaterials to the modulation of mechanical stiffness of 3D silk biomaterials.

Water soluble SF films containing different concentrations of Ca^{2+} ions were prepared by mixing degummed silk fibers and $CaCl_2$ in different weight ratio in formic acid. Then, after the evaporation of the solvent, SF films were redissolved at defined pH values. The high solubility and the rheological properties of SF protein made possible its printability using exstrusion based printing and electrospinning. Circular dichroism, Raman, IR, and UV–vis spectroscopies were used to investigate the conformational transition.

We exploited the bidirectional actuation properties of silk II for the 4D printing of two devices with different medical applications (i.e., intestinal anastomosis and intestinal distraction enterogenesis), the viscoelastic properties of silk-I like conformation for the mechanical exfoliation of light responsive nanomaterials to get photo-responsive and printable biomaterials, the development of 3D printed SF patches that trigger the biotrapping properties through the formation of silk II hydrophobic domains, and the extrusion process to facilitate the formation of liquid-crystalline ordered SF β-sheet.

In this study we report the polymorphic nature of SF. The obtained results can open the way for the development of others multifunctional devices beyond the case studies shown here. Importantly, we found that the silk I structure is the key secondary structure that promotes the dissolution of SF films in aqueous environment for the regeneration of (i) water insoluble silk biomaterials, (ii) mechanically stiff and hydrophobic patches with high β-sheet content and (iii) liquid-crystalline ordered SF with high β-sheet content in aqueous solution.

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RAPID PREPARATION OF POLYMER-BASED HIERARCHICAL STRUCTURES

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Multiphasic materials with bioinspired and hierarchical architectures could allow gathering and possibly improving the properties of starting constituents, thus currently finding application in different fields, including water remediation, sensors, biomedicine, and so on. Unfortunately, as the laboriousness of preparation tend to increase upon increasing morphological and functional complexity of hierarchical structures, the most urgent challenge is to develop rapid and possibly one-step methods, aiming to reduce costs and use of toxic/dangerous chemicals.

PCL and PLA were chosen as polymer substrates, graphene oxide (GO), carbon nanotubes (CNTs), micro- (MCF) and nanocellulose fibers (NCF), lignin were used as coating agents.

Wet electrospinning in active liquid collector was used to prepare fluffy monoliths coated with hybrid nanoparticles in one-step. A series of PLA and PCL solutions were prepared and electrospun into a coagulation bath constituted of ethanol or ethanol/water with nanoparticles dispersed. The materials were characterized from a morphological, physicochemical, mechanical point of view. Functional tests were performed to assess pollutant sorption performance and electrical responsiveness.

We produced 3D porous monoliths with tailored morphologies from macro- to nanoscale. The microstructure of the polymer substrate was designed by adjusting the compositions of spinning solution and coagulation bath, along with process parameters. Bulky or spongy polymer fibers were achieved using co-solvents or non-solvents in the liquid collector. Various coatings were designed relying on electrostatic wrapping and self-assembly of different nanoparticles. Hybrid coatings with spider leg-like architectures were attained using 2D/1D hybrid dispersions of GO-CNTs in ethanol or ethanol/water. Longer fibers as 1D fillers (e.g., GO-CNF, GO-MCF dispersed in ethanol/water) led to spider web-like architectures. Introducing 0D nanoparticles like lignin, along with 2D or 2D/1D nanoparticle dispersions, enabled shish kebab-like architectures. Combining polymer substrate microstructure and nano-patterned surfaces, imparted high mechanical robustness, tunable architecture, porosity (up to 99.5%), surface wettability (from hydrophobic to hydrophilic), making them suitable for treating wastewater contaminated with (multiple) dyes, organic compounds, and oil/water emulsions. All samples containing CNTs demonstrated highly sensitive electrical conductivity to environmental variations, showing their potential as multifunctional smart materials.

This study was carried out within the MICS (Made in Italy - circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) - MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 - D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Uion nor the European Commission can be considered responsible for them.

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PLAYING WITH THE SIZE OF GOLD TO DESIGN TAILORED CATALYSTS AND WIN THE MATCH OF METHYL-2-FUROATE SUSTAINABLE PRODUCTION

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Lignocellulosic biomass waste valorization into added-value chemicals is one of the most challenging approaches in the forthcoming concept of bio-refinery. An example is the oxidative esterification of furfural to methyl-2-furoate. Alkyl furoates find applications as flavor and fragrance component in fine chemical industry. Their production involves strong oxidizing agents to obtain 2-furoic acid, further esterified by concentrated acid in alcohol. Conversely, another method requires strong bases. In this study, Au/ZrO_2 catalysts with modulated gold size were tested by employing O_2 as benign oxidant and without any base. The nature of the Au sites depending on the particle size and the sites able to activate O_2 and methanol were investigated to establish structure-activity relationships.

Au/ZrO_2 catalysts with 1.5 wt% Au loading were prepared and submitted to final calcination at different temperature (from 423 up to 923 K). Catalytic tests were carried out under previously optimized conditions. FTIR spectroscopy of adsorbed CO, O_2 and methanol coupled with HR-TEM, CO chemisorption and DR-UV Vis spectroscopy were employed.

Catalytic tests showed that conversion increases by decreasing the Au size, while selectivity to methyl-2-furoate does not vary significantly for the catalysts containing clusters, very small particles, and particles. Upon calcination at 923 K small particles and clusters coalesce to form large particles. These features drastically decreased productivity and selectivity, but the catalyst is still active. However, if assuming that the small Au size is essential for the activity, these results cannot be explained. Both nature and role of Au sites of clusters and particles were investigated. Au clusters activate O_2 to form atomic O, whereas superoxo species are produced by either clusters or particles. Experiments wiht pre-hydrated samples revealed that Au perimeter sites at the metal-support interface play a key role in methanol activation during reaction, opening new perspectives on the design and synthesis of more performant and stable materials.

COMPOSITE MATERIALS FOR AUTOMOTIVE APPLICATIONS BASED ON RECYCLED FISHING NETS AND BIOCHAR

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Discarded fishing nets constitute a significant part of ocean pollutants (640,000 tonnes/year), accounting for 20 % of all marine activities. Giving new economic value to end-of-life fishing nets could encourage their recovery through an appropriate logistical collection system. Their reuse as raw material can reduce marine pollution and the use of petro-based plastics, particularly in the automotive sector. In this context, the present study aims to explore the recyclability of disposed fishing nets to produce more sustainable composites, using epoxidized waste vegetable oil (EWVO) as a biocompatible material. Furthermore, rice husk biochar (BC) is used as a renewable alternative to traditional carbon black due to its multifunctional characteristics as a flame retardant.

EWVO was synthesized by epoxidation of Repurpose Used Cooking Oil (RUCO) and BC was produced by pyrolysis of rice-husk. Fishing nets were collected, washed, air-dried, and characterized by FTIR and DSC analyses. Thermal analyses were performed to assess the materials' suitability for subsequent mechanical recycling and compounding by melt extrusion. The composites were produced by a single-screw extruder at 235-240°C (60 rpm, N_2 atmosphere) using different EWVO and BC amounts. Rheological analyses and tensile testing were conducted to evaluate material processability and mechanical performance compared to virgin plastics. Flame retardant characteristics of developed composites were evaluated through cono-calorimetric measurements and vertical burn tests.

The analyses conducted resulted in the identification of HDPE, polyamide 6, and polyamide 6,6 as the constituents of the gathered nets, with polyamide 6 being the predominant material. Each net was successfully reprocessed by extrusion, exhibiting similar mechanical properties to the virgin plastics. Preliminary compatibilization tests for HDPE/PA6 blends using EWVO showed that for HDPE/PA6 75/25 and 85/15 blends, the addition of EWVO at 2 phr had a satisfactory compatibilizing effect. The epoxy groups of EWVO reacted during blending with both PA6 carboxyl and amino terminal groups, resulting in oil-terminated PA6. These molecules migrate to the PA6/HDPE interphase, thereby reducing interfacial tension and improving compatibility between the polar polyamide and the hydrophobic polyethylene. This resulted in a material with improved mechanical properties compared to the blend without compatibiliser.

Composites based on recycled PA6-based fishing nets, containing 5, 10, 15, and 20 wt.% of BC, were successfully processed by extrusion. The incorporation of BC increased Young's Modulus and stress at break of PA-6 but reduced strain at break. Furthermore, preliminary cone calorimetric measurements suggest the tendency of rice husk biochar, markedly rich in silica, to induce flame retardant properties.

A SYNERGIC COMPUTATIONAL AND EXPERIMENTAL APPROACH TO CORRELATE STRUCTURE AND PROPERTIES IN CARBON DOTS

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Carbon Dots (CDs), and in particular N-doped CDs, are C-based rounded nanoparticles (diameter < 10 nm) with high emission quantum yield and large emission tunability across the visible range, depending on composition and structure. These optical properties, along with high chemical inertness, resistance to photobleaching, and biocompatibility, make CDs highly desirable for many technological purposes. However, a still open challenge is the correlation between their structure and photoluminescence. At present, the emission properties are not exclusively ascribed to a single mechanism: quantum confinement, due to hypothesized nanosized sp2 carbon core, and molecular states or surface states, due to fluorophores formation and surface traps, respectively, are both considered. In addition, the optical emission is in general excitation-dependent, suggesting the presence and possibly the interplay of more than one mechanism.

Carbon dots were prepared by solid-state synthesis of citric acid and urea in different molar ratio at 180°C at various synthesis time. Optical spectroscopy, NMR spectroscopy, XPS spectroscopy, structural and morphological analysis were considered to characterize the structure and properties of CDs. Quantum chemistry calculations were applied to model the emitting centres and their formation during the synthesis.

By changing the molar ratio of the precursors, CDs with main emission in the blue and green range can be prepared. The structural features indicate the presence of a carbon network with a large degree of disorder increased by the presence of N doping. The emission properties are related to both surface groups and molecular centers, whose formation starts from the very first minutes of the synthesis. The calculations allow ascribing the optical properties to some specific centers and to follow their genesis during the synthesis.

In these years we worked on the characterization of the role of N in CDs to ascertain how the doping modifies the structure and the optical properties of our samples aiming at correlating structure, morphology, and spectroscopic features by means of synergic experimental and computational approaches. The presentation will discuss our insights and perspectives to address the CDs' challenges and opportunities for a CD-based technology.

VALORIZATION OF BIOMASS INTO HIGH VALUE PRODUCTS: OIL-BASED COATINGS AND THERMOSETS

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The valorization of biomass into high added value applications require the development of enabling technologies that can transform it into materials with desirable performances that can credibly replace fossil materials. Here I will talk about the development of new sustainable green materials from the valorization of two oil byproducts into a thermoset that can be used as a coating or a foamed material, and in general how using only materials from biomass can be engineered together to create high value products.

A typical procedure to produce material involve the blending of ESO and Pripol in a fixed ratio of 55:45. To make freestanding materials, the mixture of the two oils is then poured into a mold. To use it as a coating, it was dissolved in ethyl acetate in different concentrations (from 1% to 15%) to control the thickness of the deposited coating. In both examples, samples cured in an oven at 80°C and a catalyst could be added to decrease curing time.

Freestanding films were produced by simple casting and curing, in a solvent-free manner, thanks to the reaction between the epoxy groups of ESO with the dicarboxylic acid groups of pripol. To this sample, large amounts of vegetable powder could be incorporated, to enhance the mechanical properties of the resulting composite. Leveraging on the possibility of moisture absorption of the vegetable biomass, fully biobased foams could be obtained without the need for high temperature post processing or the use of supercritical CO_2. Crosslinking epoxidized soy oil and Pripol as a coating on fish leather, created a nanometric thin coating that provided the durable waterproofing needed. In also shows how a high-performance waterproofing can be obtain without resorting to $–CF_3$ or silicone chemistry, or the use of nanoparticles.

Both applications show how biobased materials when engineered together can be a credible alternative for high performance materials. Foams can be created using only oils and vegetable biomass, while the coating provided excellent water resistance to fish leather, without changing the breathability, flexibility, and the microstructure of the substrate. This work demonstrates how high performing materials can be created within a green chemistry and circular economy framework.

EFFECT OF PHENOL-RICH EXTRACT FROM CHESNUT (CSW) WASTES ON THERMAL, MECHANICAL, ANTIOXIDANT AND ANTIMICROBIAL PROPERTIES OF POLYLACTIC ACID FILMS

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This research activity proposes the development, production and characterization of PLA films for food packaging sector. In this work, chestnut extract at 1, 3 and 5 wt % was used as additive. The effects of content on optical, morphological, thermal and mechanical properties of PLA based films have been investigated. In addition, migration and radical scavenging activity, antimicrobial and antifungal studies were performed, with the aim of evaluating the effect on structural and functional properties of realized food packaging systems.

A fraction obtained by water–ethanol extraction and purification/concentration by membrane technology was considered for CSW extract. CSW was characterized by a total polyphenol content of 260 ± 3 mg/g, while the most representative phenolic compounds were hydrolysable tannins, such as vescalagin (47.6 ± 0.5) and castalagin (97.7 ± 0.9). Poly (lactic acid) (PLA, 4032D) was purchased from NatureWorks. Neat PLA, PLA_1CSW, PLA_3CSW and PLA_5CSW films were realized by using a twin screw microextruder (DSM Explore 5&15 CC Micro Compounder). During the mixing, the screw speed was set at 60 rpm, with a temperature profile of 170-175-180°C throughout the three zones and a die temperature of 180°C. The films obtained following this process have a nominal thickness between 30 and 50 μm.

Results from migration tests for simulant A evidenced that for all PLA based formulations were below the migration permitted limits, with exception of PLA_5CSW. Strength and elastic modulus of films were not affected by the presence of CSW, while a reduction in terms of elongation at break was registered. The use of CSW induced antioxidant activities, inhibitions on bacterial and antifungal growth, suggested the practical and possible applications in food packaging industrial sectors.

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3D-PRINTING VIA VAT PHOTOPOLYMERIZATION: SUSTAINABLE BIOBASED RESINS CONTAINING LUMINESCENT ADDITIVES

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3D printing is a computer-aided production technique that translates virtual 3D models into customized products of desired shape, design and size, building up an object layer by layer. Compared to traditional manufacturing techniques, 3D printing is a sustainable manufacturing process, resulting in much less material waste. Among the available technologies, stereolithography (SLA) and Digital Light Processing (DLP), based on the photopolymerization of appropriate resins, offer some advantages in term of resolution over the extrusion approaches, together with the possibility to tune the final mechanical properties of the object with an accurate choice of the resins' components. Because of the increasing demand for new smart materials, the addition of specific additives to the resins can open the possibility to transfer one or more additive's properties into three-dimensional objects.

Recently, we focused our research both on the development of new photopolymerizable resins maximizing the employment of bio-based materials, and on the use of photoactive additives that, not interfering with the printing process, can produce luminescent final objects potentially useful in different fields, from textile and fashion industry to biomedical applications.

We developed a fully bio-based resin for DLP 3D printing for applications in rapid prototyping and modelling, formulated by mixing a photocurable polyester obtained from renewable resources (poly(1,3-propanediyl-co-glyceryl) itaconate-co-vanillate) with methacrylated citrate and itaconate crosslinkers to improve the printing resolution, and appropriate photopolymerization initiators and terminators.

As a proof-of-concept, photocurable inks were formulated with dyes and phosphorescent Ir(III) cyclometalated complexes and their potential applications have been demonstrated for both rigid and flexible structures with a possible outlet in the textile/fashion industry.

Subsequently, to broaden the application of 3D printing of photopolymerizable resins, we addressed our attention to the use of biocompatible and highly fluorescent additives such as carbon (nano) dots (CDs). We set up a new synthesis of red emitting CDs from renewable materials and used them in formulations to print objects with different mechanical properties to for potential applications in implantable structures.

ENHANCING NANOCELLULOSE-BASED MATERIAL PROPERTIES THROUGH INORGANIC COMPOUND ADDITION: A PATH TO ADVANCED PERFORMANCE

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The finite nature of petroleum-based materials and the phenomenon of climate change underpin the urgency of transitioning to renewable materials and eco-friendly practices. Nanocellulose (NC) materials (cellulose nanocrystals -CNC- and cellulose nanofibers -CNF-), being derived from cellulose, represent more sustainable alternatives to materials derived from fossil-fuels. The appealing properties of NC, such as its lightweight, high strength, and low thermal conductivity, together with its versatility in being easily processed into films and aerogels, make it a promising candidate for several applications, including food packaging, thermal insulation, gas absorption, etc. The main limitation in the effective use of NC, which is its poor wet resistance, can be overcome by the addition of tailored inorganic compounds with multiple activities. Specifically, water-soluble and ionic Ag(I) and Cu(II) coordination complexes have been used as reinforcing agents for NC, offering the additional possibility to impart their distinctive properties to the resulting composites.

Stable hybrid colloids were prepared by suspending CNC (4% w/w) in water, followed by the addition of the desired amount of the coordination compound (3, 4, 5% w/w, with respect to CNC). Hybrid films were obtained through solvent casting, whereas hybrid aerogels were fabricated via freeze-drying. Reference samples containing only CNC were also prepared as comparison.

The hybrid colloids, films, and aerogels were morphologically, structurally, and mechanically characterized and compared to the reference CNC samples. The CNC colloidal suspensions incorporating the Ag(I) and Cu(II) compounds showed a lower gel point with respect to pure CNC, accompanied by the appearance of birefringent textures. The homogeneous hybrid films and porous hybrid aerogels, obtained from the colloidal suspensions, exhibited an improved wet resistance with respect to the corresponding CNC reference materials.

The inorganic compounds exerted a reinforcing effect on CNC, presumably due to a synergistic ionic and chemical cross-linking action, due to the ionic nature of the complexes and to the presence of specific chemical moieties on the ligands coordinated to the metal centre. Therefore, the addition of the inorganic species to CNC results in more resistant and durable materials, with a positive effect on overall performance.

ENHANCED REDUCTIVE CATALYTIC FRACTIONATION OF RAW POPLAR WOOD SAWDUST WITH A MAGNETIC RECYCLABLE CATALYST

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Fractionation of 2nd generation lignocellulosic biomasses is an essential step for biorefinery strategies to isolate and fully exploit cellulose, hemicellulose and lignin for the production of materials, fuels and chemicals. One of the most promising strategies aimed to lignin valorisation is based on the extraction, depolymerisation and simultaneous stabilisation of this fraction towards the production of low molecular weight lignin oil through the so called Reductive Catalytic Fractionation (RCF). RCF is a catalyst dependent process capable of producing phenolic compounds and hemicellulose-derived polyols while preserving the carbohydrate cellulose pulp in the presence of a reducing agent, generally hydrogen. Supported noble metal catalysts over carbons or Al_2O_3 were found to be active; however, one major issue, often underestimated, is represented by the inefficient catalyst recovery from the fibrous cellulose pulp which limits catalyst recyclability thus impacting the economic sustainability of the entire process at larger scale.

$RuO_{2/\gamma}Fe_2O_3$ (5%wt of metallic Ru) was obtained by Incipient Wetness Impregnation (IWI) of a commercial Fe_3O_4 (sigma Aldrich, d<50nm, 98%) with an alcoholic solution of $RuCl_3 \times 3H_2O$ followed by drying at 70°C. The powder was milled and calcined at 400 °C for 3 h (ramp 10 °C/min). Catalysts have been characterized by means of XRD, porosimetry, TPR-O-R, atomic emission spectroscopy (MP-AES) and TEM-EDS.

We developed a novel magnetic catalyst based on supported ruthenium oxide over maghemite ($RuO_{2/\gamma}$-Fe_2O_3), which behave as suitable precursor of the actual, in-situ obtained, Ru/Fe_3O_4 active phase for the RCF. The performances of this system, in terms of delignification of cellulose, lignin oil yield and catalyst recovery, were compared with the one obtained with a commercial 5 wt% Ru/C, considered as a benchmark. A simple, lab-scale, magnetic recovery procedure allows to obtain around 94% of recovery efficiency after the first reaction cycle (while the liquid-liquid extraction reported in literature to recover the Ru/C catalyst only led to 10% of recovery). Ru/Fe_3O_4 allows to obtain excellent delignification efficiency, with the concomitant formation of a highly pure cellulose pulp. On the other hand, both the lower surface area and bigger Ru nanoparticles compared to Ru/C, limit lignin depolymerisation efficiency to phenolic monomers. Preliminary recyclability tests have proven the stability of our catalyst for at least 3 RCF cycles. This magnetic catalyst, never reported in literature in a RCF processes, shows great potential thanks to its good recyclability and its ability to produce very high-quality cellulose pulp together with relatively low MW lignin oil.

ENHANCEMENT OF KRAFT PAPER PERFORMANCE WITH MODIFIED PVOH COATINGS FOR SUSTAINABLE FOOD PACKAGING

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The packaging industry is moving to paper due to environmental worries about plastic pollution. Paper is biodegradable, recyclable, and compostable, but it faces challenges like hydrophilicity and high permeability, notably in food packaging. The use of biodegradable coatings can significantly improve paper properties, addressing its main limitations. In this regard, polyvinyl alcohol (PVOH) provides protection against gas permeation, resistance to external agents, and improved adhesion, owing to its film-forming ability, high barrier properties, and biodegradability. This renders PVOH coatings an interesting option for eco-conscious and functional paper-based packaging solutions.

The study deals on improving Kraft paper's overall functional performance by applying biodegradable coatings of a water-resistant and high-barrier ethylene-modified polyvinyl alcohol (m-PVOH) at different concentrations.

Kraft paper with a grammage of 100 g/m^2 supplied by Netuno Sp.z o.o. (Wojska, Poland) was coated with water-based solutions (10%, 15%, and 20% wt/wt) of Exceval AQ-4104 provided by Kuraray Europe GmbH and chemical, thermal, and functional properties of the produced structures were assessed.

Rheological analysis revealed distinct flow behaviors in m-PVOH coating solutions, with shear-thinning observed in the 20% solution due to increased m-PVOH concentration and enhanced hydrogen bonding. Coated paper samples maintained a constant thickness despite increasing grammage, suggesting permeation of coating solutions into the paper's fibrous matrix. Cobb60 values demonstrated a maximum reduction of 57% in water absorption for Kraft paper/20% m-PVOH samples, while water vapor permeability at 23°C and 50% RH remained constant across all coated samples (~ 4.0 g/ (m^2 day)), indicating enhanced resistance to both liquid and vapor water.

Air permeability resistance increased with higher m-PVOH concentrations, correlating with a rise in coat weight. Oxygen barrier properties remained constant across concentrations ranging from 573.0 to 588.4 $cm^3/(m^2$ day) at 50% RH, suggesting potential suitability for food packaging. Tensile strength of Kraft paper was maintained, with a slight improvement in elongation at break in the cross direction for coated samples. Overall, the study highlights the potential of m-PVOH coatings to enhance Kraft paper, offering a promising environmentally conscious alternative for sustainable packaging.

DIFFERENT CULTIVATION SYSTEMS FOR MORE ECO-SUSTAINABLE AND HEALTHY PRODUCTS: TRADITIONAL CULTIVATION VS HYDROPONIC SYSTEM FOR NICKEL-FREE TOMATO

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The rapidly spreading issue of Nickel Allergy has pushed agricultural companies to implement adjustments to their systems to ensure the lowest possible presence of heavy metals, in particular Nickel, in fruits and vegetables that are normally fixative to these metals. Hydroponic cultivation systems, which do not involve the use of potentially polluted soil as a means of plant growth, appear to be an effective solution to the problem of nickel allergy. With the purpose of optimizing non-soil cultivation systems, In this work, the nickel contents and main organoleptic characteristics of two tomatoes of the same species were compared, one from traditional soil cultivation and one from hydroponic cultivation and therefore labeled nickel-free.

The whole tomatoes (datterini) were cutted in small pieces, dried for eight hours in the oven at 105 °C, and ground by hand in a ceramic mortar. For the removal of organic components and the leaching of metals in solution, an acid digestion treatment was adopted for all samples. 50 ml of an acid mixture HNO_3:$HClO_4$ (4:1) were added to beakers containing 2 grams of each sample. The beakers were placed on a heating plate at 250 °C until at least 90% of the solution evaporated, which was subsequently diluted with double-distilled water, filtered into 20 ml flasks, and made up to volume with double-distilled water. Tests for the TOC content was carried out on the treated samples, as well as analysis for the detection of the Nickel content using ICP-OES. The two types of tomatoes were also compared from the point of view of mechanical properties via puncture tests.

Tests on the TOC content of samples treated with acid digestion all give results below 150 mgTOC/l. This indicates that the acid digestion treatment provides almost complete removal of the organic matrix of the sample. From the ICP analysis, the nickel content detected in "datterini" tomatoes from traditional cultivations is higher than nickel-free ones which, according to the labelling, contain less than 0.01 mgNi/kg. Puncture tests revealed no differences in firmness between the two types of tomatoes.

The acid digestion treatment carried out as a preparation for the analyzed samples is effective for the detection of Nickel via ICP. All recommended experimental parameters were respected, including a TOC value <150 mg/l, so the results are reliable within the precision limits of the instrument. This study highlights the effectiveness of soil-less cultivations compared to traditional ones in terms of reducing the nickel content in products. The results obtained will be included in a broader research work on the technical and environmental optimization of hydroponic and aeroponic cultivation systems, and its effects on the characteristics of the final products.

MONTMORILLONITE/GRAPHENE OXIDE AND CHITOSAN-BASED THIN FILMS WITH HIGH OXYGEN BARRIER AT HIGH HUMIDITY

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The oxygen barrier properties of packaging materials play a key role in preserving food products. Thus, high-barrier packaging solutions are requested to ensure quality and safety maintenance during food shelf life. Inorganic thin films (i.e. SiO_x or Al_xO_y) present ultralow gas permeability and high transparency, but they suffer from pinholes and defects and are mainly fabricated with expensive/complex processing methods. Layer-by-layer (LbL) assembly is a deposition technique that prepares multilayer thin films by alternately exposing a charged substrate to oppositely charged polyelectrolytes or particles. LbL-deposited coatings have the advantage of using water-based processes in ambient conditions and obtaining nanometric control over thickness. In the present work, two types of anionic nanoplatelets, graphene oxide (GO) and Na^+-montmorillonite (MMT), were alternately used as anionic layers with chitosan (CH) to fabricate nanobrick wall barrier nanocoatings via LbL.

A corona-activated PET film was alternately dipped into CH, MMT, CH, and GO mixtures. Each dip step was followed by washing with DI water and blow drying to remove any loosely adherent material. The thickness of thin films was measured on Si wafer with a P6 profilometer. Oxygen transmission rate (OTR) was tested following ASTM D-3985 using an Oxtran 2/21 ML instrument at 23 °C under 0% RH and 90% RH, by MOCON Inc.

Growth of the assemblies was monitored using profilometry, observing a linear thickness growth as a function of layers deposited. The TEM cross-sectional images highlighted the high level of nanoplate orientation. The 123 nm thick CH/MMT/CH/GO thin film reduces the oxygen permeability of PET from 17.6 to 0.21×10^{-16} cm^3 cm cm^{-2} s^{-1} atm^{-1} in dry conditions, and from 13.4 to 0.42×10^{-16} cm^3 cm cm^{-2} s^{-1} atm^{-1} at 90% RH. UV-vis spectroscopy reveals a reduction of light transmittance in the visible spectrum from 98% for 179 μm PET films to 84% from CH/MMT/CH/GO-coated PET films.

This reduction of OP by one order of magnitude, both at 0% to 90% RH, is likely due to the dense multilayer structure with high loading of oriented nanoplatelets observed from TEM images, which generates a tortuous permeation path for oxygen and water molecules. These nanocoatings also show suitable transparency for the application Therefore, the simultaneous use of these two anionic nanoplatelets in an LbL-assembled structure proved to be an effective strategy for improving the barrier performance of chitosan-based coatings at high humidity.

DESIGN OF DUAL-EMITTING NONAROMATIC FLUORESCENT POLYMERS THROUGH THERMAL TREATMENT OF L-GLUTAMIC ACID AND L-LYSINE

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The study of absorption-emission features of non-aromatic amino acids is an emerging field that has attracted attention. UV-Vis absorption and emission in proteins is a well-known phenomenon that is generally attributed to the presence of aromatic or, more generally, conjugated groups. Recent experimental and computational studies have shown absorption and emission in the visible range for proteins lacking conjugated groups and from polymers obtained by thermally treated glycine and lysine. Optical properties of such systems have been explored by thermally treating another non-aromatic amino acid as glutamic acid.

Glutamic acid has been homopolymerized in a furnace at 240°C for 5h and copolymerized with lysine in the same condition with different molar ratios. The brown-black solids thus obtained have been dispersed in water, sonicated and centrifugated. Supernatant was collected and filtered using a 0.45 um syringe filter and the dialyzed for 24 h replacing water once, finally the solution has been freeze-dried resulting in a brownish powder.

Polypeptide-like branched polymeric structures have been synthesized via the thermal treatment of L-lysine and L-glutamic acid. Thermal polymerization produces branched polymers whose close packing between the chains favors intramolecular charge transfer. The polymers exhibit two-color centers with emissions peaking at around 380 and 450 nm. The relative homopolymers, polyglutamic acid and polylysine, exhibit, upon thermal polymerization, only one emission at 450 nm. The second emission is observed only when the two amino acids are copolymerized. The polymerization kinetics and, thus, the incorporation and abundance of the precursors into the final polymers affect their spatial conformation, which is starkly correlated to the relative molar ratios of the two precursors. The structural characterization has shown that the increase of fluorescence is strictly correlated with the mutual spatial proximity of oppositely charged moieties, which favors charge transfer between the side chains of the precursor amino acids.

The fluorescent emission is related to charge transfer and recombination processes that involve acceptor and donor groups, and occasionally intermediates groups. The single emission of the homopolymers and the second center of the copolymers peaking at 450 follow a similar charge transfer/recombination route while the first emission center peaking at 390 of the copolymers can be explained by a different mechanism.

ELECTROSPUN BACTERIAL CELLULOSE SCAFFOLDS COATED WITH ELECTROSPRAYED CHITIN NANOFIBRILS FOR EARDRUM REPAIR

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Repairing tympanic membrane (TM) perforations in chronic otitis media poses significant challenges in otologic surgery due to infection and inflammation hindering self-healing and graft stability. This study explores a novel nanotech-based tissue engineering approach for developing a functional TM patch to enhance wound healing and tissue regeneration. The proposed bio-based patch utilizes nanoscale materials such as bacterial cellulose (BC) electrospun fibers and electrosprayed chitin nanofibrils (CNs) derived from fishery biowaste. Green solvents, including 1-Butyl-3-methylimidazolium acetate ([Bmim]OAc) for BC and water/acetic acid for CNs, are employed for processing. Ionic liquids, being non-volatile, offer potential solutions to the poor solubility of cellulose in conventional solvents.

BC, sourced from Gluconacetobacter xylinus, underwent rheological analysis to achieve optimal viscosity (3% w/w BC/solvent) for electrospinning. An electrospinning setup featured a rotating collector immersed in distilled water for solvent removal from fibers. Parameters included a 50 rpm rotating collector, 9 cm distance from the needle tip (21G×3/4"), 0.3 mL/h flow rate, and 23 kV voltage. CNs (0.52 w%) in aqueous acetic acid and water underwent morphological, physicochemical, and mechanical characterization. Cytotoxicity tests utilized L929 mouse fibroblasts, while rabbit skin irritation tests were conducted in vivo. In vitro regenerative assessments employed HaCaT cells and HUVECs.

Optimizing electrospinning parameters and using dimethylsulfoxide (DMSO) as a co-solvent yielded continuous, uniform, partially aligned BC fibers (228 ± 77 nm), exhibiting cellulose type II crystalline structure. BC electrospun fiber mesh (90 ± 14 μm thickness, Young's modulus 2.48 ± 0.62 MPa) was enhanced with CNs via electrospray to boost immunomodulatory and regenerative properties. CN presence promoted antimicrobial activity by upregulating beta-defensin-2 expression in HaCaT cells and modulating pro-inflammatory cytokines, rendering the patch promising for TM perforation wound healing. Cytocompatibility studies using L929 fibroblasts, HaCaT cells, and HUVECs confirmed compatibility of both uncoated and CN-coated BC fiber meshes. In vivo rabbit skin tests showed no irritation after 24 hours.

The combination of electrospun BC nanofibers with electrosprayed CNs demonstrated a promising approach for the development of an ideal bio-based and sustainable TM patch that addresses the challenges faced by current graft materials. This innovative biomaterial has the potential to significantly improve the outcomes of myringoplasty procedures, by providing both optimal regenerative capabilities and functional support for TM healing.

NEW ANTIBACTERIAL DRESSINGS FOR THE TREATMENT OF SURGICAL AND NON-SURGICAL WOUNDS IN SPINE SURGERY

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Wound infections are common issues in orthopaedics, following surgery, percutaneous implants and prolonged wear of orthotic devices, and require antibiotic treatment, hospitalization, and readmission. To promote their healing, dressings are needed, capable of absorbing exudates and promoting tissue regeneration. Electrospun patches have shown promising in addressing these needs and can adapt to complex shapes, so they can be easily coupled with prostheses/orthoses. However, prevention of infection remains unmet, and the applicability of antibiotics-based strategies is limited by bacterial resistance. Here, we propose innovative antimicrobial electrospun dressings, exploiting essential oils, which show broad spectrum antibacterial efficacy and high biocompatibility. We start from the encapsulation of tea tree oil (TTO) in poly(ethylene oxide), PEO, for immediate and burst release (post-surgical patch), and in polycaprolactone, PCL, to achieve a longer release profile (for prolonged use in transcutaneous implants and orthoses). After optimization of the electrospun patch characteristics, we explore a library of antimicrobial oils (thymol, lavender, turmeric, ginger, lemon, cinnamon, citronella), to target different microbial communities.

PEO-TTO patches are developed with different TTO concentrations (3/5/7.5/10 w/w). Optimized electrospinning parameters are selected based on patch morphology (SEM), the amount of TTO effectively embedded and its stability over time (>14 days, UV-VIS spectrophotometry). After optimization, PCL-TTO is electrospun with the optimized TTO content.

For each oil, the minimal inhibitory concentration is calculated against Escherichia coli ATCC® 8739™ and Staphylococcus aureus ATCC® 6538P™. After embedding in the PEO and PCL patches, oils release profile is studied and their antibacterial efficacy is tested (n=3), by evaluating the planktonic growth (4h, 8h) and adhesion to the substrate of the aforementioned bacteria.

PEO and PCL patches (w/wo oils) show negligible defects and a suitable morphology. Despite their volatility, oils can be efficiently incorporated in PEO and PCL. All TTO-patches show high inhibition of the planktonic growth of S. aureus (% reduction vs patch without oil: 98% PEO, 96% PCL) and a moderate effect on E. coli (72% PEO, 81% PCL), consistently with the different capability to permeate the membrane of gram-positive and gram-negative bacteria. TTO-patches also significantly inhibit bacterial adhesion, for both strains. These results are oil-dependent, as different oils exert different efficacy against gram + and gram – strains, paving the way for personalized medicine in infection.

Electrospun essential oils-loaded antibacterial patches are successfully developed, obtaining high stability over time and antimicrobial efficacy, thus appearing promising for application in wounds healing.

HUMAN H-CHAIN FERRITIN: A MULTITASKING SYSTEM FOR THE DESIGN OF NANOSTRUCTURED BIOMATERIALS

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Protein self-assembly is a mechanism leading to formation of supramolecular organizations useful to construct nanostructured biomaterials. Among the different proteins used to this purpose, human H-chain ferritin (hHFt) emerges as highly versatile multitasking system. Here, we report a detailed study of hHFt spontaneous and non-spontaneous self-assembly abilities that unveiled its potential, ranging from drug delivery system to building-block for the development of functional amyloids. Indeed, the hollow cage structure makes it suitable for the loading of small bioactive molecules, as metallodrugs or peptides, thanks also to a new efficient disassembly/reassembly protocol we recently developed. On the other hand, stressful experimental conditions can drive hHFt subunits to assemble into well-ordered fibrils. Moreover, hHFt fused to selected epitopes is a represents a versatile scaffold for the development of new vaccines.

Appropriate hHFt constructs were designed, expressed in *E. coli* and purified as homogeneous nanocages. Loading with cargos was performed by partial disassembly with SDS followed by reassembly. hHFt fibrils formation, prompted by incubation at 90°C at low pH, was monitored by ThT fluorescence binding assay. Structural characterization of the protein assemblies was performed by X-ray, TEM, SEM and Cryo-EM.

Comparative structural data (TEM, X-ray, cryo-EM) showed that hHFt nanocages correctly reassemble, even in the presence of bioactive molecules, which seem trapped in the bulk. The biological tests highlighted that, as the native hHFt, the reconstituted nanocage is safe for cells, not showing any kind of toxicity, while the drug-loaded hHFt is toxic only on cancer cells. When converted into fibrils, β-sheet rich aggregates are formed whose size, estimated by TEM and SEM images, reaches micrometre size.

By using an appropriate disassembly/reassembly protocol, we report here that hHFt can efficiently trap biomolecules inside its cavity with high efficiency. The presence of the cage ensures structure and function preservation of the loaded molecules and protects healthy cells, selectively delivering drugs to tumour cells, thus confirming its potential as nanocarrier. On the other hand, the ability of ferritin to turn in fibrils and the understanding of its aggregation mechanism open the possibility to design new functional materials with improved properties.

ADVANCED STIMULI RESPONSIVE NANOSTRUCTURES: MESOPOROUS SILICA CORE@SHELL ARCHITECTURES WITH DAHLIA-LIKE MORPHOLOGY AS INNOVATIVE SMART DRUG DELIVERY PLATFORMS TO FIGHT COLORECTAL CANCER

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Nanoparticles can be used to precise targeting and controlled release of therapeutic agents redefine cancer treatment paradigms. Mesoporous silica nanoparticles (MSNs) have gained considerable attention due to their physical-chemical characteristics: large surface area and pore volume, biocompatibility, high loading capability, facile surface functionalization and targeting functions. Here, core@shell nanostructures (SiO_2@MSNs), consisting of non-porous silica core and dendritic mesoporous silica shell were designed, synthesized and loaded with a chemotherapeutic agent, namely 5-fluouracil (5-FU), for the targeting and treatment of colorectal cancer. Furthermore, the surface of these nanostructures was functionalized with polyacrylic acid (PAA), selected for its pH sensitivity, and with Frizzled-10 (FZD10) antibody, for creating a tumor-targeted delivery system based on pH-based stimuli. Luminescent carbon dots were also incorporated into the SiO2@MSNs to achieve optical traceable nanostructures used for in vitro imaging study. Luminescent SiO_2-MSNs were obtained by means of a biphasic soft-templating strategy, by using cetyltrimethylammoniumbromide (CTAB), as cationic surfactant and tetraethylorthosilicate (TEOS) as silica precursor in alkaline conditions. Physical-chemical characterization and drug loading and release assay were performed. To assess their biological properties, different in vitro studies of cytotoxicity, cell proliferation and uptake were conducted on human colon epithelial, non-metastatic and metastatic human colorectal adenocarcinoma cells. SiO_2@MSNs with dahlia-like morphology were characterized by average size of 200 nm (σ%= 4%), a relevant colloidal stability in aqueous media, large pores ranging from 4 to 20 nm and a drug loading of 15%. Drug release assay was performed at different pH conditions to verify the pH-responsive efficiency of the nanostructures and the results highlighted that the amount of released drug was higher at pH>5 (in colon environment) for the expansion of PAA, thus opening the silica pores, than at pH<5 (in gastric environment), when the polymer, coiling up, closed the pores. The in vitro studies demonstrated the high biocompatibility of the nanostructures, their targeting ability of different CRC cell lines and the presence of the carbon dots allowed to optically monitor their cell uptake. The conclusive results demonstrate the successful development of pH-responsive FZD10 antibody-functionalized SiO_2@MSNs for potential use in targeted treatment of CRC through oral or rectal administration of 5-FU, showcasing promising candidates for clinical application.

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DESIGN OF SMART PLATFORMS FOR APPLICATIONS IN TISSUE REGENERATION AND BIOMARKER DETECTION

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Nowadays, the design of tissue engineered constructs and reliable in-vitro models show great potential to overcome the limitations of conventional surgical, pharmacological and diagnostic approaches especially in the treatment of cardiovascular diseases and cancer. In this context, the Horizon-Europe REBORN project aims to restore hearth functionality after myocardial infarction through the design of a piezoelectric polymeric patch capable of providing controlled in-situ drug release. In parallel, the PRIN-2022-PNRR FOCAL project proposes the integration of fiber-optic sensors into polymeric electrospun substrates to develop in-vitro models suitable for the detection of tumoral biomarkers.

In the case of the cardiac patch, electrospinning was exploited to process hybrid polymeric formulations combining polyvinylidene-fluoride (PVDF) with different ultrasound (US) responsive carriers using a rotating collector to promote fibre alignment. The resulting patches were comprehensive characterised also testing the ability to release different drugs with and without US stimulation. Electrospinning was also used to design different biopolymer-based cell-adhesion substrates suitable for the integration of fiber optics, where different surface mofications of metal-oxide films were explored to improve fiber sensitivity.

For the cardiac patch, PVDF-based hybrid formulations were optimised and processed by electrospinning resulting in aligned nanofibrous membranes characterised by great flexibility and piezoelectric properties. Hydrophilicity of the surface was guaranteed by oxygen plasma treatments while the ability of the system to deliver different drugs was proved by HPCL analysis. As for the design of nanostructured in-vitro models, different polymeric nanofibrous subtrates were produced by means of electrospinning while nanopatterning of metal-oxide films proved to lead to increased fiber-optic sensitivity.

The processing of piezoelectric polymers combined with drug-eluting carriers by electrospinning has shown great potential in the design of smart cardiac patches supporting tissue regeneration and in-situ pharmacological treatments. Moreover, electrospun nanofibrous membranes represent promising cell-adhesion substrates, where fiber-optics can be integrated as sensing elements to promote the detection of biomarkers for the design of advanced diagnostic devices.

PREPARATION AND CHARACTERISATION OF FDM 3D-PRINTED BIOCOMPOSITE SCAFFOLDS FOR BIOMEDICAL APPLICATIONS

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Polyhydroxyalkanoates (PHAs) are thermoplastic polyesters synthesized by bacteria through the fermentation of sugars or lipids. PHA medical devices have been extensively studied in scientific research and clinical trials for various applications, including tissue engineering, drug delivery, and vascular stents.

In this work, polyhydroxybutyrate (PHB) was chosen as a naturally-derived biopolymer matrix, suitably formulated by adding a bio-based, biocompatible plasticiser obtained by the reaction between levulinic acid and glycerol, and an innovative bioactive phosphate glass added in different amounts (5, 10, and 20 wt%), to produce bioactive bioresorbable porous scaffolds for tissue engineering applications. The scaffolds were fabricated by fused deposition modelling (FDM) process, a 3D printing technology that enables customisable structural and functional solutions.

The scaffolds were obtained in cylindrical geometry with regular and homogeneously distributed pores ranging from 300 to 400 μm in size. Electron microscopy showed good dispersion and distribution of the bioglass particles in the polymer matrix, which did not affect the characteristic temperatures of the polymer matrix for the various compositions as detected by calorimetric analysis. Mechanical characterization tests indicate that the stiffness and strength of the scaffolds remained constant regardless of their composition, while a dependency on their construction characteristics was confirmed.

The interconnected macro-porosity of the scaffolds should ensure high transport capacity for colonization and subsequent cell growth by diffusing nutrients, oxygen, and other factors, essential for tissue regeneration. The scaffold bioactivity is expected to improve with the inclusion of phosphate bioglass, while the addition of the bioplasticiser is known to increase the window of processability of the PHB matrix.

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3D PRINTING OF LIQUID CRYSTAL ELASTOMERS AS ARTIFICIAL MUSCLES

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Liquid Crystal Elastomer (LCE) are very promising smart materials that, combining the behaviour of a liquid crystals with those of elastomeric polymers, can find application in several fields from stimuli-responsive actuators to molecular machines. LCEs can change their shape in response to external stimuli in a reversible way giving the possibility to convert this energy to a mechanical work. 3D Direct Ink Writing (DIW) allows the structural alignment of LCEs to be programmed (given by shear stresses generated by the printing nozzle), thereby controlling their contractile direction in response to external stimuli. In this communication, we describe the preparation and characterization of LCE obtained by DIW. Both materials that are responsive to temperature and light irradiation have been prepared by adding an azo-benzene dye in the ink formulation. Photo-actuation tests have been conducted to enlarge the possible application of as light fueled artificial muscle.

Inks are synthetized via Michael thiol-acrylate reaction, mixing a diacrylate mesogen (RM82), a dithiol and a photo-switch molecule. The LC mixture is printed in a range of temperature where it showed a nematic phase then cured using a 385nm UV lamp. LCEs thermo-mechanical performances were characterized through Dynamic Mechanical Analysis (DMA) and Differential scanning calorimetry (DSC). Finaly, the LCEs were photo-actuated in a homemade set-up with a light source of 470nm (blue light) to measure the tension developed under the light-irradiation.

The ink's nematic-isotropic transition temperature change depending on dye concentration. LCEs show an elastomeric behavior with a Young Modulus in the range of MPa. The developed tension from photo-actuation test varies from 1.2 kPa to 13.4 kPa according to light intensity and irradiation time.

This study demonstrates how DIW 3D printing can be fundamental to produce LCE films, classically obtained through an infiltration process through an LC cell, which cannot have a precise control over the thickness obtained. Moreover, DIW 3D printing can be used to obtain materials with the desire molecular alignment in an automated process in a fascinated way.

To date, these results are the first that show photo-actuations of LCE obtained with 3D printing in activation times in the scale of milliseconds, obtaining value of tension developed (kPa) comparable with of those of human myocardium.

SHORT ORAL

IRON (III) ANCHORED ON SILICA NANOPARTICLES AS CURING ACTIVATOR FOR RUBBER VULCANIZATION

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Rubber vulcanization is the main industrial process used to crosslink rubber polymer chains through sulfide bridges and produce nanocomposites with high mechanical properties. A fast and efficient curing process requires an activator, usually ZnO. However, the low affinity of ZnO towards rubber entails its high consumption to achieve a good distribution in the polymer matrix, leading to non-negligible release in working condition and environmental impact. Therefore, replacing Zn as an activator has become an important issue. In this work, Fe@SiO_2, constituted by Fe(III) sites anchored on silane-functionalized SiO2 nanoparticles (NPs), is proposed as an activator to substitute ZnO in the rubber vulcanization.

Fe@SiO_2 was produced through a two-step synthesis: i) SiO_2 NPs were functionalized with (3-aminopropyl)triethoxysilane (APTES) in toluene; ii) functionalized SiO_2 was dispersed in ethanol containing $Fe_2(SO_4)_3$ in order to anchor Fe(III) on the surface. Fe@SiO_2 was characterized through TGA, FT-IR, ICP-OES, EPR, XPS analyses and SE Microscopy. Fe@SiO_2 was tested as an activator in the vulcanization of isoprene rubber nanocomposites prepared in a Brabender mixer and cured at 170°C. Dynamic mechanical tests were performed in a Rubber Process Analyzer (RPA).

Fe@SiO_2 activators with amount of Fe(III) ranging from 0.25% to 5.5% were synthesized. The presence of iron on silica surface was confirmed by EDX mapping in SEM. EPR showed a signal at $g \sim 4.3$ and one at $g \sim 2.0$, the latter increasing in intensity at the highest loading of Fe(III). Fe@SiO_2 exhibited a faster kinetics and a most efficient vulcanization process respect to ZnO conventionally used in the industrial process.

The EPR signals at $g \sim 4.3$ and $g \sim 2.0$ correspond respectively to isolated Fe(III) centres and coupled Fe(III) centres, possibly via electrostatic or proper chemical interactions, e.g., oxygen bridging. This latter increases with increasing amount of iron but no difference in reactivity occurs between isolated and coupled iron species, since the vulcanization performance depends only on the total amount of iron. The fast kinetics exhibited by Fe@SiO_2 compounds is likely a consequence of the immediate availability of Fe(III) centers on the silica surface to react with the curatives. Concluding, Fe@SiO_2 was able to outperform ZnO as a curing activator in terms vulcanization degree, with equal amount of Fe and Zn, demonstrating to be a valid and sustainable alternative to ZnO in rubber vulcanization.

MECHANICAL PROPERTIES OF SINTERLESS 3D PRINTED SILICA GLASS: A MULTI-TECHNIQUE COMPARATIVE STUDY

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Silica ceramics are essential in aerospace due to their superior thermal resistance and lightweight, enhancing thermal protection and fuel efficiency. Their durability under extreme conditions ensures the safety and longevity of aerospace vehicles and components. Therefore, studying novel routes for their synthesis and precise understanding of their mechanical properties is significant. Building upon the innovative work by Bauer et al., in which a novel approach utilizes drastically reduced process temperatures for the development of silica glass upon 3D printing micro-templates, this study explores the nanomechanical properties of the 3D printed silica glass and compares them with conventionally fabricated silica using lithography and Focused Ion Beam (FIB) milling. We examine the elastic modulus, hardness, and fracture toughness of silica pillars with average radii of 2.65 μm (3D print), 2.58 μm (lithography), and 2.51 μm (FIB), through Continuous Stiffness nanoindentation and the pillar splitting method (G200 nanoindenter with a cube-corner tip).
We determine the fracture toughness of 3D printed silica (0.667±0.058 $\mathrm{MPa}\sqrt{\mathrm{m}}$), aligning with established literature values (ranging from 0.58 to 0.78 $\mathrm{MPa}\sqrt{\mathrm{m}}$) and comparable to lithography-fabricated silica (0.629±0.014 $\mathrm{MPa}\sqrt{\mathrm{m}}$). In contrast, FIB-milled silica pillars do not exhibit unstable crack propagation, which is likely attributable to FIB-induced damage.
Moreover, given their lower induced-stress intensification factor during indentation, we found similar densification behaviors when splitting with Berkovich tips, leading to enhanced fracture toughness, with values reaching around 3 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for silica samples from all fabrication techniques. We further explore the impact of thermal treatments on the fracture toughness of silica pillars, revealing how processes like partial glass conversion, induced by treatment at 1000°C, affect their mechanical properties. This study corroborates Bauer et al.'s findings on the feasibility of sinterless 3D printing of silica glass at lower temperatures. It broadens our understanding of silica's mechanical attributes across various manufacturing methods. These insights are crucial for advancing microsystems technology and nanophotonics, where the mechanical integrity of silica is paramount.

FABRICATION AND ELECTROCHEMICAL CHARACTERIZATION OF Co-FREE ELECTRODE MATERIALS FOR SOLID OXIDE CELLS

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The development of high performing and stable electrocatalysts for intermediate temperature solid oxide cells (IT-SOCs) stands a key factor to promote the upscaling of this technology. IT-SOCs has the working temperature between 600°C to 800°C which engineers the way to use different fuels and provides high efficiency and kinetics.

In this work, innovative perovskite-based air electrode materials such as the Co-free $La_{0.7}Sr_{0.3}Cu_{0.15}Fe_{0.85}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$ for conventional and symmetrical IT-SOCs were synthesized through the sol-gel method. The resulting powders were characterized by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). Electrochemical impedance spectroscopy (EIS) measurements were conducted in electrolyte-supported and complete button cells to test their performance electrolysis and fuel cell operating mode. The compatibility of the synthesized powders with different electrolytes was also investigated.

The EIS measurement was performed in the range 1MHz to 0.1Hz. The effect of partial pressure on the performance of the electrocatalyst was also investigated. Low polarization resistance values in the 0.01-0.1 $\text{ohm}\cdot\text{cm}^2$ range were obtained for both materials. The measured current-voltage characteristics on the complete cells also showed competitive performance with the state-of-the-art materials in both operating modes.

The data analysis showed that $La_{0.7}Sr_{0.3}Cu_{0.15}Fe_{0.85}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Fe_{0.9}Mo_{0.1}O_{3-\delta}$ can provide high electrochemical performance in terms of polarization resistance if compared to other Co-free materials. The mobility of copper at the operating temperature should be taken into account for the stability of $La_{0.7}Sr_{0.3}Cu_{0.15}Fe_{0.85}O_{3-\delta}$ over time. The distribution of relaxation times analysis subsequently demonstrated the impact of oxygen partial pressure and temperature. The results showed that increasing the oxygen partial pressure from 10% O_2 to 100% O_2 at constant temperature, decreases the polarization resistance, suggesting that a superior gas diffusion inside the electrode materials is achieved. Additionally, the effect of increasing temperature from 600°C to 700°C at constant partial pressure leads to a reduction of the polarization resistance. Moreover, both materials were deposited on two different solid oxide electrolytes (Gd-doped ceria and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.8}O_{3-\delta}$) and found compatible with them at the operating temperature.

MESOPOROUS Ni/Zr MIXED OXIDES FOR THE CATALYTIC DRY REFORMING OF METHANE

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Due to the high specific surface area, pore structure, and wide pore size, mesoporous metal oxides are often used as catalysts in several industrial processes. Among the different synthesis procedures, coprecipitation methods, also template assisted, represent an easy way to prepare mesoporous materials with different compositions and chemico-physical properties. In this respect, two mesoporous NiO/ZrO_2 materials were prepared by a coprecipitation procedure and characterized. The samples were tested as catalysts in the Methane Dry Reforming, which allows the use of two greenhouse gases (CO_2 and CH_4) to produce syngas.

Two NiO/ZrO_2 samples (Ni 10 wt%) were synthesized by a coprecipitation procedure performed with (NiO/ZrO2_CTAB) and without (NiO/ZrO_2) cetyltrimethylammonium bromide (CTAB) as templating agent. The materials were characterized by different techniques in terms of composition, structure, morphology, texture, and redox properties. The H2 treated samples were catalytically tested in the temperature range 600 700°C.

Both catalysts are characterized by type IVa N_2 physisorption isotherms and type H_2 hysteresis loops, typical of mesoporous materials. The use of CTAB leads to higher specific surface areas, with a value of 149 m2/g even after calcination at 700°C. At this temperature, nanocrystals of tetragonal ZrO_2 with an average diameter of 6 and 7 nm are estimated for NiO/ZrO_2_CTAB and NiO/ZrO_2, respectively, whereas reflections of very low intensity are visible for NiO. H_2-TPR profiles highlight the presence of NiO species strongly interacting with zirconia. Both the catalysts are found highly active and stable within 5 hours on stream.

Being able to promote strong NiO-support interactions, the coprecipitation procedure adopted allows preparing catalysts with very high specific surface area and NiO dispersion, even after severe calcination treatments. CO_2 conversion values are slightly higher than those of CH_4, suggesting that side reactions can occur to some extent. Despite this, the H_2/CO molar ratio is always very close to 1:1, especially at the highest temperature investigated. Among the two samples, slightly better performance is obtained with NiO/ZrO_2_CTAB, suggesting the role of CTAB in promoting the resistance of the catalyst to sintering phenomena and carbon deposition possibly occurring during the process.

PRODUCTION, CHARACTERIZATION, AND APPLICATION OF NANOSTRUCTURED SPINEL FERRITE MOCVD FILMS FOR WATER SPLITTING

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Spinel nano-ferrites are active for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), through combined effects of electronic interactions between cations at octahedral and tetrahedral sites, as well as through the impact of different M^{2+} cations. The easily production, good chemical stability, and redox activity together with the abundance in nature, non-toxicity and low cost of the constituent elements make ferrites desirable materials. Several ferrites have been studied to be applied in water splitting devices, such $CaFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, and $ZnFe_2O_4$.

MOCVD process was used to produce $NiFe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$ films. Commercial iron(III) precursor [Iron(III)tris(2,2,6,6-tetramethyl-3,5-heptanedionate), $Fe(tmhd)_3$] and the synthetized β-diketonate precursors, $M(tta)_2tmeda$ (Htta = 2-thenoyltrifluoroacetone, tmeda = N,N,N',N'-tetramethyl-ethylendiamine, M=Ni, Co, Zn) were employed. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis were used to assess the precursors thermal features. XRD measurements were used to investigate the crystalline film formation. FE-SEM was used to evaluate films morphologies. EDX quantitative analysis was used to evaluate the cations' stoichiometric ratio. XPS was employed to assess the cations' oxidation state. FIB-SEM was used to produce lamella specimens then analysed with HR-TEM. Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) analysis were used to evaluate the HER and OER activity.

XRD measurements confirmed the production of polycrystalline ferrite phase on silicon, MgO and Ni-foam substrates. EDX quantitative analysis assessed the 1:2 stoichiometric ratio between the divalent cations. XPS confirmed the ferrite phases presence and evidence iron oxides contaminations in certain samples. HR-TEM measurements confirm the presence of a polycrystalline phase, in agreement with the XRD data. Preliminary HER and OER measurements of $NiFe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$ samples on Ni-foam show promising results.

MOCVD processes successfully guarantee deposition of ferrite films on various substrates. XRD, HR-TEM and XPS assess the phase formation and evidence the presence of small amount of amorphous iron oxides in some samples. FE-SEM allows the evaluation of films, having cubic shape morphology, with a thickness around 300-400 nm. Overpotential, Tafel Slope and Rct values obtained through LSV and EIS demonstrate the applicability of the films deposited on Ni-foam in water splitting.

UNDERSTANDING THE WORKING MECHANISM OF THERMALLY PROMOTED *IN SITU* CATION EXCHANGE AT THE SOLID STATE IN A TRANSMISSION ELECTRON MICROSCOPE

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In recent years, the demand for novel nanomaterials has surged due to their diverse applications in optoelectronics, photonics, and catalysis. Various synthetic methods have been developed to obtain nanocrystals (NCs) with precise control over composition, crystal phase, and morphology. Among these methods, post-synthetic transformations such as cation exchange (CE) reactions have emerged as potent tools for fine-tuning NC properties. Understanding the mechanisms underlying CE reactions is crucial for guiding novel nanostructure designs.

This study builds upon previous work demonstrating CE reactions at the solid state using *in situ* transmission electron microscopy (TEM). Utilizing a microelectronic mechanical system (MEMS)-based in situ heating holder, experiments were conducted to monitor CE reactions between Cu_2Se nanocrystals and CdSe nanowires (NWs) with varying crystal structures. High resolution scanning TEM (HRSTEM) and STEM-based chemical mapping techniques were employed to observe the early stages of CE reactions and probe local chemical composition. All the calculations in the atomistic CE model were performed by classical molecular dynamics (MD) using a suitable force-field (FF) capable of reproducing mutual interactions between Cu atoms and CdSe in both crystal structures.

Observations revealed that copper expulsion and subsequent CE occur at different temperatures depending on the crystal structure of the CdSe NWs. For hexagonal CdSe NWs, CE initiates at 400°C, while for cubic CdSe NWs, CE begins at 125°C. Additionally, a partially reversible CE process was observed in cubic CdSe NWs below 250°C. MD simulations provided insights into the fine mechanisms, activation energies and probabilities of CE reactions for different crystal structures.

The combined experimental and theoretical approach sheds light on the mechanisms governing CE reactions at the solid state. The study demonstrates how varying the crystal structure of nanoparticles influences CE reaction kinetics and outcomes. These findings contribute to a deeper understanding of CE processes and provide valuable insights for the rational design of nanomaterials with tailored properties under novel conditions. In conclusion, this study extends previous in situ TEM investigations of CE reactions, offering new insights into the role of crystal structure in dictating CE reaction kinetics and behavior. The experimental and theoretical findings provide a comprehensive understanding of CE mechanisms and highlight the importance of environmental conditions in shaping CE outcomes.

SELF-HEALING BIO-CONCRETE: DEVELOPMENT AND CHARACTERIZATION OF AN INNOVATIVE GREEN MATRIX

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Self-healing concrete emerges as a revolutionary solution for autonomous crack repair, obviating the need for human intervention. This study delves into the potential application of bacteria derived from common brewer's yeast to induce self-repair. Additionally, we explore the formulation of an eco-friendly mix design, incorporating natural waste such as mussel and clam shells. This research aims to redefine industry standards, promoting sustainable solutions in the infrastructure sector.

The experimental investigation focused on developing and evaluating a novel approach to self-healing concrete. Ordinary Portland cement served as primary binder, accompanied by fine and coarse aggregates. To facilitate autonomous crack repair, different concentrations of bacteria derived from brewer's yeast (Saccharomyces Cerevisiae) were incorporated into the concrete mix. Additionally, an eco-friendly mix design was crafted by introducing heated, treated, and finely crushed mussel and clam shells in different proportions, partially substituting natural aggregates. Mechanical properties were systematically assessed through 28-day compressive strength tests, with comparisons made to control mixes containing limestone sand or gravel.

Replacing traditional cement with seashells, specifically mussel and clam shells in bio-concrete yielded a robust compressive strength of approximately 25 MPa. Mixes incorporating 5%, 10%, and 15% seashell replacements consistently met the 25 MPa target at 28 days, with a marginal decrease observed at 20% replacement. Moreover, heat-treated seashells enhanced the cement paste by incorporating $Ca(OH)_2$ and $CaCO_3$, reinforcing the material and restricting pore size. The seashells' chemical composition, particularly the heightened $CaCO_3$ content, closely mirrored essential Ordinary Portland Cement components, positioning them as effective substitutes. Additionally, the seashells served as a calcium source, synergistically activating the self-healing mechanism of brewer's yeast. This led to calcium carbonate production, requiring minimal water for yeast activation. The inclusion of yeast not only prolongs the setting time to around 36 hours at 15°C but also triggers the formation of calcium carbonate crystals. These crystals serve a dual purpose, initially decreasing the material's porosity. Following the introduction of water, yeast activation takes place, actively participating in the bio-concrete's self-healing mechanisms.

The evolution of an advanced biocement, aligned with modern sustainability imperatives, stands as a groundbreaking achievement in construction. The chemical synergy between mussel and clam shells, coupled with brewer's yeast, triggers a transformative process, resulting in resilient and enduring concrete, boasting inherent self-healing capabilities. This innovative biocement diminishes CO_2 footprints, offering a promising avenue for eco-friendly and sustainable construction practices.

EFFECT OF CALCIUM HYDROXIDE INNOVATIVE TREATMENT ON THE PROPERTIES OF SISAL FIBERS AND THEIR GEOPOLYMER COMPOSITES

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Geopolymers are nowadays known as environmental friendly building materials, showing good mechanical properties, resistance to hostile environments and high temperatures. The main weakness of these materials is the fragile nature of the matrix, which limits their use in several industries. In order to overcome this issue, the incorporation of synthetic or natural fibers represents a possibile choice. In particular, natural fibers can be used as reinforcement of cement and geopolymer matrices, thanks to their low density, quite high specific mechanical properties as well as biodegradability and large availability.

The main aim of this paper is to investigate how an innovative and eco-friendly treatment of sisal fibers can enhance the mechanical performances of fiber reinforced geopolymers thanks to the enhancement of the fiber-matrix adhesion. In particular, sisal fibers were soaked in a 2 wt% aqueous solution of calcium hydroxide for 24, 48 and 72 h at 25°C. All geopolymeric samples were made by using metakaolin as precursor, activated using a 7M KOH solution and a potassium silicate powder. River sand (2 mm nominal diameter) was used as aggregate. In particular, metakaolin was initially mixed with potassium silicate powder and river sand (mix ratio 1:0.5:2). Afterwards, KOH solution was added to the mix to allow the geopolymerization. Fiber reinforced geopolymer composites were manufactured by replacing 2 wt.% of aggregate with raw and treated sisal fibers.

Chemical and morphological analyses were carried out on sisal fibers to evaluate the effectiveness of the proposed treatment. Specifically, the changes of functional groups on fibers surface have been evaluated by Fourier transform infrared analysis (FTIR). Thermogravimetric analysis (TGA) and scanning electron microscope (SEM) observation were performed to investigate the thermal and morphological behaviour of sisal fibers. Overall, all these tests have shown that the proposed treatment represents a useful alternative to traditional alkaline treatments (i.e., mercerization). Furthermore, the mechanical performances of unreinforced and reinforced geopolymer materials were evaluated by performing compression, flexural and indirect tensile tests. The experimental results showed that the mechanical performances of geopolymer composites are influenced by the fiber treatment time duration.

Overall, the proposed treatment is proven to be an effective technique to remove non-cellulosic components from sisal fibers, despite it slightly reduced their mechenical properties. Furthermore, it was found that the improved homogeneity and superficial roughness of natural fibers, in addition to the removal of surface impurities, improve the adhesion with the geopolymer matrix.

SURFACE ACTIVATION OF MEDICAL-GRADE TITANIUM DISCS BY CHEMICAL AND PHYSICAL OXIDATION PROCESS FOR THE DEPOSITION OF A BIOCOMPATIBLE FILM

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Titanium and its alloys are often used in load-bearing implants (e.g. knee and dental prostheses), because they are bioinert materials with excellent mechanical properties and good corrosion resistance. The surface roughness of implants can be modified by mechanical, chemical and physical treatments to improve the interaction between the material surface and tissues. The aim of this study is to develop a method involving the functionalization of suitably modified medical grade titanium materials with bioactive molecules (silica and layered double hydroxide) to induce a process of osteogenesis and inhibit the formation of bacterial films.

Surface modification of the samples was carried out according to two different strategies: chemical and physical. The first treatment involves immersing the samples in strong oxidizing solutions such as 30% H_2O_2, $TiCl_4$ and 1:1 H_2SO_4/H_2O_2 solution, while the second involves oxidation by plasma spray at atmospheric pressure.

The surface activation of the discs involves generating a surface with a strong propensity for the expression of hydroxyl groups, which are useful for binding silica, produced by a Stőber process, to which fluorinated Zn_2Al-LDH was added.

Characterization of the samples (SEM/EDX, micro-Raman, micro-IR) allowed us to investigate the morphology of the sample as-is and activated and to evaluate the degree of dispersion and adhesion of the silica-LDH coating, before and after immersion of the discs in an ultrasonic bath. Finally, using ImageJ software, the main surface roughness parameters were calculated.

Analysis of the untreated discs under the SEM microscope showed a surface with different types of contaminants, probably due to the processing of the samples themselves. After oxidative treatments, the percentage of contaminants decreases significantly until they disappear in samples treated with the 1:1 solution H_2SO_4/H_2O_2 and plasma spray. The microscopic technique also made it possible to assess the degree of adhesion of the silica-LDH film before and after the immersion of the discs in an ultrasonic bath. Plasma spray-activated discs showed a greater adhesion of LDH particles than the other samples analysed. Two-dimensional mapping (SEM/EDX, micro-Raman) was performed on these samples to study the distribution of the two phases in the coating, showing good integration between them. Surface roughness was assessed on chemically and physically activated samples. Samples treated with plasma spray and piranha-like solution show negative roughness values (Rsk), which tend to minimise the healing time.

POLYDOPAMINE COATING FOR LIPOSOMES: A POTENTIAL ALTERNATIVE TO PEGYLATION FOR APPLICATIONS IN BIOMEDICAL FIELD

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Polydopamine (PDA) is a biomimetic polymer obtained throughout the self-oxidation and self-polymerization of the dopamine in water under oxygenated and slightly alkaline conditions. The unique features of a PDA, its high biocompatibility and post-functionalization possibilities have triggered an growing interest for biomedical applications. Liposomes, consolidated nanocarriers for drug delivery applications, can be coated with PDA to broaden their application potential. PDA even seems able to overcome the risk factors of the PEGylated polymers, such as adverse immunological events, which encourage its use as PEG alternative for liposome stabilization.

PDA-coated liposomes (Lipo@PDA) were prepared and fully characterized from a physico-chemical point of view. The biological response of Lipo@PDA and Lipo@PEG was evaluated by studying the protein corona (PC) in FBS, the hemolytic response with the red blood cells from the human plasma and the cytotoxicity with respect to human H441 cells. Lipo@PDA and Lipo@PEG were loaded with camptothecin for the treatment of colorectal cancer. In vitro intestinal permeability and anticancer activity using HCT 116 cell-based 2D and 3D (spheroids) models were assessed.

Proteomic analysis revealed high homology between the PC of Lipo@PDA and Lipo@PEG. From a qualitative point of view, the most abundant proteins were Apoliprotein A-I, Alpha-1-antiproteinase, Albumin, Serotransferrin. As for the hemolytic response, it was possible to stay within the 5% red blood cell lysis safety threshold by modulating the concentration and thickness of the PDA shell. Both kinds of liposomes showed a similar cytotoxicity behavior. Fully biocompatible Lipo@PDA vesicles can be obtained by reducing the thickness of the PDA coating. Drug release from camptothecin loaded Lipo@PDA was slower than that from Lipo@PEG and consistent with long-reaching colorectal drug delivery. Both polymers conferred sub-diffusive behaviour to liposomes in mucus surrogate and allowed a mild increase (up to roughly 2.5-fold) in epithelial drug permeability as compared to free camptothecin. PDA-coated liposomes were over 2-fold more cytotoxic to HCT 116 cell spheroids than the free drug.

Lipo@PDA showed an interaction with serum proteins similar to that of Lipo@PEG and a hemolytic and cytotoxic behavior dependent on the thickness of the PDA coating. When tested for oral administration of anticancer drugs, Lipo@PDA shown to increase epithelial permeability of camptothecin. The mucopenetrability of Lipo@PDA was also similar to that of Lipo@PEG. Overall, PDA-coating seems to be a promising strategy for improving the properties of liposomes intended for both sistemic and oral administration of drugs.

DEVELOPMENT OF SUSTAINABLE ANTIMICROBIAL FILMS TO EXTEND FRUIT AND VEGETABLE SHELF-LIFE

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The increasing global population and the growing consumer's demand for nutritious and healthier products, along with environmental concerns, are driving researchers and manufacturers towards more sustainable food production and preservation methods, where the use of bio-based packaging materials and circular economic processes find large approval. Nowadays, the demand for fresh fruits and vegetables is significantly increasing, food post-harvest horticulture crops preservation represents a challenging issue, which looks at cutting by 2030 half per capita the food waste worldwide at both the retail and consumer level. Indeed, food losses and deterioration can occur at different stages from crops production to food supply chain, including post-harvest conditioning and warehousing. In this context, the use of extracts from plants and food-waste biomasses offers attractive options to achieve proper coating formulations that can both reduce the burden from fossil-resources and promote a biobased economy.

The following materials have been used to produce blown films: Poly (lacti acid) (PLA) Luminy LX175, Poly(butylene succinate-co-adipate) (PBSA), Joncryl ADR 4469 chain extender, bees wax, chitin and chitosan. The materials were firstly, twin screw extruded compounded; the obtained granules, after drying, were processed by film blowing. The obtained films were firstly mechanically (tensile, tear and Elmendorf tests) and thermal characterized (DSC test). The antimicrobial properties were evaluated according to ISO 22196:2011. Finally, the fruit shelf life and film seal ability were evaluated.

Interesting result have been obtained. The addition of the bees' wax improved the chitin and chitosan dispersion without affecting the thermal properties and the film processability. As far as concern the mechanical results the addition of the active molecules, due to their stiffness, decreased the film elongation and increased the film elastic modulus. However, despite of this ductility decrement, a good film stretch ability (>200%) was obtained. In particular, the formulation with chitosan is interesting for its very good antimicrobial activity also accompanied good results in shelf-life tests. This formulation in fact, only caused a lower mass loss of the fruit products, but significantly extended the shelf-life; even up to 17 days in the refrigerator and almost a week out of the refrigerator.

CuMgAl LAYERED DOUBLE HYDROXIDE AS ELECTROCATALYSTS FOR ONE-POT REDUCTION OF CO_2 TOWARDS C2 PRODUCTS

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In the context of green energy transition and CO_2 emission reduction, developing efficient catalysts for the electrocatalytic conversion of carbon dioxide (CO2ER) to high-value products is crucial. Layered Double Hydroxides (LDHs) stand out as promising materials due to their versatility and biocompatibility. By introducing redox-active cations, conductive LDHs with high surface area and CO_2-exchange capability can be synthesized at low cost. Moreover, a streamlined electrodeposition method enables the direct fabrication of LDH films onto conductive electrodes. This approach allows for precise tuning of the LDH composition, enhancing its catalytic performance. Leveraging these advantages, tailored electrocatalytic systems based on Cu, Mg, and Al LDHs demonstrate remarkable efficiency in producing acetic acid through CO_2 reduction in a single step.
This study introduces novel electrocatalysts based on CuMgAl Layered Double Hydroxides (LDHs) synthesized onto a carbonaceous gas diffusion layer (GDL). The catalysts were deposited using a one-pot potentiodynamic technique with a 30 mM solution of nitrate salts for each cation, and characterized using XRD, SEM-EDS, and various electrochemical methods. Evaluation was conducted in an H-type cell with 0.3 M $KHCO_3$ as the supporting electrolyte in both cathodic and anodic compartments, along with Pt gauze and Ag/AgCl (KCl sat.) as counter and reference electrodes. Electrode performance was assessed through potentiostatic CO_2 reductions at -0.4 V vs RHE for 1 hour, a potential previously identified for selective acetic acid production. Performance comparisons were based on acetic acid productivity and Faradaic yields.
After synthesis, the electrocatalysts underwent thorough microscopic and spectroscopic analysis, revealing the formation of LDH structures as thin layers with high electrochemical active surface areas with an intimate contact between a nanostructured ternary CuMgAl LDH and Cu^0/Cu_2O species. Electrochemical tests and comparison with Cu/CuO without LDH showed that all LDH-based catalysts facilitated the one-pot formation of acetic acid, with approximately 100% selectivity at low potentials. The CuMgAl 2:1:1 LDH/CP system exhibited the best performance, surpassing productivity reported in the literature under similar conditions.
The findings highlight the effectiveness of the synthesized CuMgAl LDH-based electrocatalysts in converting CO_2 into acetic acid. with the Cu^+/Cu^0 redox couple playing a significant role. The superior performance of the CuMgAl 2:1:1 LDH/CP system highlights the importance of catalyst composition optimization. These findings suggest promising prospects for LDH and Cu^0/Cu^+ species synergy in maximizing CO_2 conversion efficiency into valuable C2 products.

OPTIMIZATION OF PROCESS PARAMETERS FOR THE PRODUCTION OF POROUS SYSTEMS BY 3D PRINTING FOR CONTROLLED RELEASE

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The possibility of combining the versatility of 3D printing with the simplicity of salt leaching emerges as a promising approach in the production of porous systems, with process, environmental and economic advantages. In this direction, systems of variable morphologies and porosity can be produced for a wide application range, such as capsules for controlled release.
The raw materials used were Nylon 6 as a matrix, and common sodium chloride as a porogen agent, with three different granulometries. Ny6/NaCl 30/70%wt blend was extruded into a filament suitable for FDM. Small capsules were printed and leached in water in order to obtain porous devices. Filaments and printed devices were characterized from a morphological, physico-chemical and functional point of view. Methylene blue was used as a model molecule to verify the device capability to control release. Fertilizer was subsequently used as compound widely used in agriculture that may harm the environmental equilibrium if not adequately dosed. SEM images of filaments and printed devices shows a good and predictable distribution of porogen and pores; the variation in surface roughness due to the presence of salt/pores causes a variation in WCA. The physico-chemical characterization of filaments shows no changes in the typical peaks of Ny6 after mixing with NaCl and leaching, nor changes in crystallinity; mechanical and rheological properties change after mixing, with an increase in complex viscosity and a general stiffening of the material. Leached devices maintain good mechanical properties in compression, in dry and in wet conditions. Furthermore, when filled with a generic model molecule, they show predictable release kinetics that can be adapted to needs.
The predictability of filament and pores morphology can be attributed to the absence of cluster formation and/or fragmentation of the porogen during processing, which confirms the versatility of the process. No chemical or crystallinity variations are observed, so mixing of polymer and porogen does not cause degradation of the former. The variation in mechanical and rheological properties, therefore, can be attributed to physical interactions between matrix and porogen. Despite the stiffening of filaments, they remain printable; the printed devices not only maintain good mechanical properties, despite the high percentage of porosity, but they are also able to containe and predictably release substances, as the pores appear interconnected.

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$FeSO_4$ AND $FeCl_2$ FUNCTIONALIZED BACTERIAL CELLULOSE THROUGH IN-SITU AND EX-SITU METHODS

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Bacterial cellulose (BC) is attracting the interest of the more recent research as a remarkable versatile biomaterial employed in a wide range of applications, including food packaging, biomedical, flexible electronics, and engineering fields in general. The present research deals with the investigation of the potential attitude to functionalize two specific strains of bacterial cellulose (K2G30 and K2G44) derived from Komagataeibacter xylinus with iron.
Ex-situ and in-situ approaches have been applied to both strains, and different amounts (0.05 – 0.10%) of a $FeSO_4$ and $FeCl_2$ mixture were employed as sources of Fe, as well as different environmental conditions (sonication time) for the ex-situ method. This approach has been developed through a combined mixture design, in order to limit the number of experimental tests needed. In addition, through this statistical approach, mathematical models have been developed with predictive power to forecast the possible amount of Fe particles in the BC depending on the ex-situ functionalization conditions. The morphology and structure of functionalized BC were investigated through electron microscopy coupled with semi-quantitative analysis, FTIR spectroscopy, and X-Ray diffraction.
Results of the in-situ method suggest that the type of bacterial strain has a key role in determining the morphology of the sample, as a smoother surface can be detected for the bacterial strain K2G30 with respect to the more heterogeneous K2G44. Functionalized K2G44 is characterized by the presence of a spherical phase that has an increasing average diameter from 1 to 10 µm, by moving from 0.05% to 0.10% of FeSO4. As expected, by increasing the Fe concentration in the broth culture, also the Fe into the bacterial cellulose increases from 6.06% to 8.42% for the bacterial strain K2G44. On the opposite, the bacterial strain K2G30 needs a concentration of 0.10% to be functionalized, having the highest value of Fe around 6%. Regarding the ex-situ methods, the significant factors for each model assess that all the chosen factors (bacterial strain, $FeSO_4$ content, $FeCl_2$ content and sonication time) in single and in interaction must be taken into account to better describe the final response in terms of film quality and Fe amount.

THE ROLE OF SOL-GEL NANOCOATINGS IN THE CONTEXT OF ANTIBACTERIAL/ANTIVIRAL ADVANCED HIGH-TRAFFIC SURFACES

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The COVID-19 pandemic prompted a reevaluation of surface hygiene, leading to an increased focus on antimicrobial coatings. Sol-gel methodologies, known for their durability and cost-effectiveness, have emerged as a leading technology. MIRIA EU project aims to advance sol-gel technologies, utilizing nanoparticles like silver or copper to enhance safety in various settings and contribute to infectious disease management strategies.

Five thin films were deposited via bar coating on glass substrates starting from silicon-based hybrid organic-inorganic sol-gel formulations. The formulations varied in the organosilicon additives and the presence of nanoparticles. This study focused on assessing the mechanical and wear properties through three primary testing methodologies: nanoindentation, scratch, and wear testing. Nanoindentation was performed with KLA G200 Nanoindenter in Continuous Stiffness Measurement mode to extract elastic modulus and hardness of the films. Abrasive wear tests followed the UNI-EN1071-6 standard, and scratch resistance was assessed with the same Nanoindenter, configured for nano-scratch testing with a rounded cone tip and lateral force measurement. The antibacterial efficacy against Staphylococcus aureus was evaluated according to ISO22196:2011 standard. Advanced microscopy techniques were employed to observe microbe-surface interactions.

The coatings exhibit a smooth surface with roughness (Sa) in the range of 10 nm; cross-sections performed reported a thickness between 100-200 nm. The coatings' wear performance, evaluated through abrasive wear tests, demonstrated their enhanced wear resistance compared to the uncoated glass substrate. Two deconvolution models were employed for processed nanoindentation data, allowing the determination of the hardness and the elastic modulus of the films with a confidence bound of 95%. The H/E ratio index of the elastic strain to failure is significant. A direct correlation is observed between the trend of the critical load Lc2 (cohesive failure of the film) and the trend of H/E among different samples.

The results obtained for the samples reveal promising characteristics, including reduced friction coefficients, enhanced resistance to abrasive wear, and consistent nano-coating. These attributes position them as viable candidates for applications requiring durability. However, the mechanically tested coatings, devoid of nanofillers, did not exhibit successful antibacterial performance. Nonetheless, these preliminary analyses have been crucial in determining the fundamental characteristics of the coatings and identifying the optimal combination for adding nanofillers with antibacterial properties. Specifically, promising antibacterial results were achieved with a coating containing copper oxide nanoparticles, which demonstrated significant antimicrobial activity, achieving a 3 log (99.9%) reduction after a 24-hour contact period.

CUTICLE-LIKE MORPHOLOGY OBTAINED VIA SOL-GEL SYNTHESIS

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Partial fluid restitution caused by improper packaging design represents a main cause of beverage and food waste. One of the main strategies to tackle this problem has been the deposition of hydrophobic coatings on the innermost layer of cans and plastic bottles, often relying on oil-derived polymers. In nature, fruits, vegetables, and leaves are protected by an extracellular membrane, known as cuticle, providing hydrophobicity and transpiration capabilities. The present work aims at developing a hybrid coating with hydro-repellent properties by introducing a nature-derived hydroxy fatty acid, 16-Hexadecanoic acid (HHA), in a classic sol-gel route.

Hybrid coatings of silica and hydroxy fatty acids have been prepared via sol-gel synthesis and deposited by rod coater on corona-treated substrates. TEOS and GLYMO have been selected as network forming and network modifiers, respectively. The coating's morphology has been studied by SEM while the barrier properties were investigated via standardized instrumentation. The coating's structure and bonding were assessed by EDS and FT-IR analysis. Lastly, TGA and DSC analyses were conducted to assess the specimen's thermal behavior.

Coated BOPP and PET samples are characterized by an opaque but homogenous surface. Preliminary analysis of the coating's morphology showed a close resemblance with the typical plant's cuticle whilst for increased glycerol content the presence of silane spherulite structures was detected. Hydro repellency has been showcased by the rough structure, yet the presence of micro-cracks in the coating's network hinders potential barrier capabilities. EDS and IR spectroscopy demonstrate the presence of HHA crystals in the hybrid system instead.

The development of sustainable solutions to reduce the environmental impact of packaging and food waste has become of critical importance. In this context, bio-inspired hydrophobic coating represents an alternative and green solution to reduce fluid waste in packaging application. A rough morphology which closely resembles plant's cuticle with hydro-repellency capacity has been successfully obtained by incorporating HHA during the sol-gel synthesis. Interestingly, DSC analysis demonstrate that HHA crystalize during synthesis, leading to possible scenarios involving co-polymerization with glycerol. Moreover, the silica spherulite embedded in the coating represents a novelty structure which need to be further investigated and exploited. Crack-free coatings can be obtained by increasing the solution solid content to potentially gain barrier functionality.

PREPARATION AND CHARACTERIZATION OF PVA NANOFIBERS MEMBRANES BY HEAT ASSISTED SOLUTION BLOW SPINNING

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PVA nanofibers have gained attention in biomedical applications due to their unique properties such as water solubility, biodegradability, and biocompatibility. Controlled release is a widely studied application. However, their highly hydrophilic nature causes dissolution upon contact with aqueous media, limiting sustained release. Traditional methods to overcome this involve costly thermal or chemical treatments, posing environmental and health risks. This study introduces a rapid and eco-friendly method for stabilizing PVA nanofibers using a modified Solution Blow Spinning (SBS) process.

Polyvinyl alcohol (PVA) was dissolved in distilled water at 95°C for 4 hours. chlorhexidine (CHX) and/or graphene nanoplatelets (GNP) were added to polymer solution at 2 wt% and 1 wt%, respectively. Nanofiber membranes were produced using heat-assisted Solution blow spinning technique (HASBS). HASBS apparatus included a compressed air source, syringe, electronic injection pump, and spinning setup with concentric nozzles. The fibers were collected on a heated aluminum foil collector. Process parameters: polymer solution flow rate of 45 mL/h, air pressure of 0.5 MPa, needle-to-collector distance of 20 cm, spinning time of 15 min, collector temperature of 200°C, and chamber temperature of 60°C.

Neat PVA system exhibited smooth and homogeneous fibers with unimodal diameter distribution and average diameter value of 1 μm. The presence of GNP in PVA/GNP caused the formation of fiber bundles and an increase in average diameter value by 50%. Adding CHX to PVA led to the formation of homogeneous fibers with some beads and, contextually, a 20% decrease in the average diameter if compared to neat PVA. The contextual presence of drug and the nanoparticles in PVA/CHX-GNP system induced the formation of homogeneous and defect-free fibers. However, in this case, there was no formation of fiber bundles.

The formation of fiber bundles in the PVA-GNP system may be due to solution instability during processing, consistent with findings from previous studies. GNP presence increased fiber diameter, likely due to its known effect of increasing polymer solution viscosity. Conversely, chlorhexidine typically decreases viscosity, but this effect was mitigated by GNP presence. All systems exhibited wavy fibers, uncommon in conventional SBS nanofibers. This wavy pattern may result from PVA fiber stabilization during deposition onto the heated collector.

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CYCLODEXTRIN NANOPARTICLES CONTAINING TERPYRIDINE MOIETIES: EXPLOITING METAL COORDINATION TO MODULATE ANTICANCER PROPERTIES

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Cyclodextrins (CDs) are versatile building blocks to fabricate therapeutic platforms, owing to water solubility, biocompatibility, biodegradability and ease of modification. In the present work, CD nanoparticles (NPs) have been chemically modified with chelating moieties of terpyridine (pβCDtpy). NPs can form metal complexes decorated with a biotin-tpy derivative (TpyBio). Biotin can recognise sodium-dependent multivitamin transporter (SMVT) overexpressed in cancer cells.

A cross-linked β-CD polymer (84 kDa, 54 CD cavities) was functionalized with 3-([2,2':6',2''-terpyridin]-4'-yloxy)propan-1-amine (TpyNH$_2$) by a condensation reaction with EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide and HOBt (Hydroxybenzotriazole). Cu (II) and Fe (II) complexes with pβCDtpy (pβCDtpy-M^{2+}) or (pβCDtpy-M^{2+}-TpyBio) were prepared by mixing a metal ion solution with the ligands and characterised by UV-Vis spectroscopy. The antiproliferative activity of ligand, binary and ternary complexes was investigated in glioblastoma cancer cells (GIN28) with PrestoBlue assay.

Terpyridine moieties were conjugated with a cross-linked polymeric βCD scaffold. The 1H NMR spectra showed the presence of 48 tpy units linked to CDs.

To study the complexation properties of pCDtpy, we carried out the titrations of pβCDtpy with M^{2+} salt solutions (M = Fe, Cu). The UV-Vis spectra of complexes showed a band at 313 nm due to the conformational change from the trans/trans to cis/cis conformation of tpy in the metal complexes. The spectra upon the stepwise addition of Fe^{2+} showed the characteristic band at 558 nm due to the metal-ligand charge transfer (MLCT) transition. The spectra changed to an M^{2+}/pβCDtpy 24 ratio, confirming the NMR data. Furthermore, the biotin derivative of Tpy was added to form ternary complexes (pβCDtpy-M^{2+}-TpyBio, M = Fe or Cu).

The inhibition of cell proliferation was investigated in GIN28 cells. All the compounds showed IC50 values lower than Temozolomide (TMZ, IC50=214.15 μM), a common drug used to treat glioblastoma. However, the most promising system was the ternary complex in the presence of copper (pβCDtpy-Cu^{2+}-TpyBio), whose IC50 was about 0.33 ±0.09 μM.

ADSORBENT COMPOSITE MATERIALS FOR HEAT STORAGE AT LOW TEMPERATURE

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Environmental sustainability and energy saving are critical aspects to address global challenges related to climate change, resource depletion and environmental degradation. Great attention, therefore, is paid to improving the use of thermal energy by increasing the efficiency of current technologies, reducing dissipation and promoting accumulation. The accumulation and recovery of thermal energy through the adsorption/desorption of water vapor on microporous solids is a technology that has already reached good scientific maturity, as demonstrated by the numerous articles published even recently. In this work we propose the synthesis and characterization of composite materials specifically tailored for the recovery of thermal energy from low-temperature sources.

Adsorbent composite materials have been obtained starting from liquid mixtures of hydrophilic microporous materials, such as silica gel, zeolites, hydrated salts, with polymeric precursors and subjected to different synthesis techniques, electrospinning, photopolymerization, thermoforming, for the optimization of the adsorbent and mechanical properties of composites. The samples were characterized by SEM microscopy, thermogravimetry, adsorption capacity measurements and mechanical strength tests.

Composites of microporous material and polymeric matrix, suitable for the adsorption of water vapor for the recovery of thermal waste at temperatures below 120 °C have been produced. The forming technology used significantly influences the final properties of the composite. The microfiber morphology obtained with electrospinning is the one that has demonstrated the greatest vapor permeability while photopolymerization has allowed the mechanical properties to be improved at the expense of the adsorption capacity of the microporous material.

The efficiency of storage systems for the recovery of low-temperature thermal energy is significantly influenced by the properties of the adsorbent material in terms of quantity of adsorbed vapor and efficiency of the thermal exchange during the accumulation and regeneration phases. For this reason, it is very important to use materials with high water adsorption capacity organized in configurations that minimize mass and heat transfer resistances. The prepared composites allow using the flexibility of technologies related to polymeric materials and therefore optimizing the configurations of adsorbent beds in thermal storage systems. With an appropriate choice of the microporous material, the polymeric component and the forming technology, it is possible to adapt the functional and structural characteristics of the adsorbent composites to the needs of the different thermal storage systems.

A SUSTAINABLE MULTILAYER COATING WITH CURCUMIN-DERIVED PIGMENT AND RICE BRAN WAX ADDITIVE

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This research highlights the versatile attributes of curcumin-based pigment and rice bran wax, both selectively chosen as natural additives in the creation of multifunctional multilayer coatings for wood.

The impact of these two environmentally friendly materials on the structure of the composite layers was assessed by conducting observations using scanning electron and optical microscopy. Furthermore, the effects of the two green additives on the paint's durability were assessed by exposing the samples to UV-B radiation and continuous thermal fluctuations. Infrared spectroscopy measurements, color analysis studies, and adhesion tests were employed to gauge the impact of the environmentally friendly additives. Moreover, the coatings' ability to act as barriers was assessed through liquid resistance tests and water absorption evaluations to understand the contributions of curcumin and rice bran wax powders. Finally, the hardness and resistance to abrasion of the coatings were examined to assess how the additives influenced the mechanical properties of the coatings.

The investigations unveiled the striking color properties of curcumin, which added a unique yellow hue to the paint. Furthermore, incorporating rice bran wax into an additional top layer affected the surface characteristics of the samples, resulting in reduced roughness and gloss of the coating. When exposed to UV-B radiation, the coating underwent noticeable and consistent color changes due to significant photodegradation of the curcumin powder. However, the preservative qualities of the polymer matrix remained unaffected by the presence of both curcumin and rice bran wax additives, demonstrating their remarkable stability under thermal stresses. The tests evaluating liquid resistance demonstrated that neither curcumin nor rice bran wax adversely affected the protective capabilities of the paint. These additives did not introduce significant irregularities in the acrylic matrix, thereby preventing excessive liquid absorption. Moreover, the inclusion of wax in the coatings improved water repellency, indicating an enhancement in the barrier properties of the layers. Significantly, the wax agent had a reinforcing effect, mitigating potential mechanical wear and tear from abrasive stresses. Therefore, the combination of curcumin and rice bran wax presents intriguing possibilities as natural additives for wood coatings. Their application results in vivid coloring and distinct aesthetic qualities in the paint while enhancing the coating's resistance to water and abrasion.

BIO-CHEMICALS-BASED RECYCLING FOR HARD-METAL WASTES VALORISATION

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Since 2011, W and Co have been listed among critical raw materials by the European Union due to their high and increasing economic importance and the risk related to their supply. W and Co demand in Hard Metal (HM) production and other applications, heavily affects their criticality and price. For these reasons, the use of secondary resources represents a more sustainable approach, following a circular economy model encouraged by European Directives. A long-lasting and fruitful collaboration between the University of Cagliari and F.I.L.M.S. SpA is addressed to design a combined carbothermal and chemical process able to provide, in few steps and low environmental impact recovered WC-Co powders of a manufacturing grade. In this work, a new chemical recycling process based on the use of low-cost, bio-derived, and bio-degradable organic acids is applied to a selection of semifinished products of a pyrometallurgical process on HM scrap specifically involving three steps: Oxidation, Reduction, and Carburization (OXR).

Leaching process is conducted on HM powders with a selection of organic acids in aqueous and non-aqueous solution by varying operative conditions such as temperature, pH solution and liquid-to-solid ratio. Leaching solution is analysed trough an ICP-OES to determine leaching efficiency and treated powders are characterised by XRD, FT-IR and elemental analyses.

Organic acids represent appealing leaching agents for metals for their complexing nature. Furthermore, they can be obtained from agro-industrial substrates through low-cost biological processes. They proved to be efficient leaching agent in metal dissolution from HM powders. Particularly, onto WC-Co materials, they behave as selective leaching agent towards the metal binder. Differently, onto oxidized materials, both W and Co are dissolved at high rates. This lowers the selectivity of the approach but activates W reactivity towards low-hazard and easy-to-handle reactants. Good quality HM has been obtained by sintering the recycled powders. A deep microstructural characterization of the obtained recycled materials is in progress, to compare the properties of the HM provided by the coupled OXR-Chemical process.

MULTICATALYTIC ELECTRODES FOR REVERSIBLE SYMMETRIC SOLID OXIDE CELLS (r-SSOCs)

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Among the up-and-coming technologies, reversible solid oxide cells (r-SOCs) represent a efficient way to store and convert energy using a single device. The interchangeability between SOFC and SOEC operation is the key aspect and the development of performing, versatile and robust electrodes must be pursued. A multi-purpose catalyst would allow for the design of a reversible symmetric cell (r-SSOC), reducing fabrication and maintenance costs. Such a flexible electrode material must comply with the requirements of both SOC electrodes, namely ensuring high performance in a wide pO_2 range: catalytic activity towards fuel oxidation and H_2O/CO_2 reduction, electronic and ionic conductivity, long-term stability, tolerance to carbon deposition. In this work, platinum doping at the B-site of a lanthanum strontium ferrite has shown remarkable versatility, making it able to operate as oxygen exchange catalyst and fuel electrode material.

5 mol% Pt was successfully doped at the B-site of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ through citrate-solution combustion method. The effect of Pt-doping on the parent perovskite structure was evaluated by X-ray powder diffraction (XPRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TG) and oxygen temperature-programmed desorption (O_2-TPD). $La_{0.6}Sr_{0.4}Fe_{0.95}Pt_{0.0}$ $O_{3-\delta}$ (LSFPt) performance as a SOC air electrode was evaluated in terms of electrical conductivity and polarization resistance as a function of temperature and pO_2. The rate-limiting steps of oxygen exchange reactions were investigated by means of equivalent circuit modelling (EC) and distribution of relaxation times (DRT) on electrochemical impedance spectroscopy (EIS) data. LSFPt structural evolution after thermal treatment in 5% H_2/Ar was screened.

Results are compared to the undoped parent perovskite (LSF) and to a commercially available state-of-the-art 20 mol% Co doped (LSCF). 5-mol% Pt inclusion enhanced the ORR/OER activity, lowering the LSF area-specific resistance by 29% and approaching LSCF performance. After reduction, Pt-Fe finely distributed exsolution provided the fuel electrode with catalytically active sites. LSFPt symmetric H_2-SOFCs and CO_2-SOECs, displayed 720 $mW\cdot cm^{-2}$ power density and 1.66 $A\cdot cm^{-2}$ current density at 1.6 V, respectively, at 850°C. Endurance tests on LSFPt-based r-SSOCs demonstrated a remarkably stable SOFC/SOEC cyclability and a steady current density output for over 370 h in 50:50 CO_2:CO at 850°C.

IONIC LIQUIDS-BASED INNOVATIVE SYNTHESIS OF Fe-Ru BIMETALLIC CATALYSTS FOR CO_2 HYDROGENATION: A SUSTAINABLE APPROACH TOWARDS NET-ZERO FUEL PRODUCTION

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The use of a bifunctional catalysts capable of facilitating both the Reverse Water Gas Shift (RWGS) and Fischer–Tropsch reactions is crucial for efficiently converting CO_2 into lower olefins (C2-C4), which is essential for sustainable chemical production and LPG. Recent research highlights the cost-effectiveness and efficacy of Fe-based catalysts, especially Fe/Ru bimetallic catalysts, in improving olefin selectivity. In this study, the application of ionic liquid solvents assumes a pivotal role, serving as nanosynthetic templates for the synthesis of Fe/Ru bimetallic catalysts. Unlike traditional solvents, ionic liquids offer enhanced stability to Metal NanoParticles (MNPs) owing to their elevated ionic charge, polarity, and supramolecular network. This innovative methodology enables precise modulation of stable MNPs synthesis, indispensable for ensuring stable catalytic performance in CO_2 hydrogenation. Ionic liquids exhibit superior selectivity to hydrocarbons (HC) compared to conventional techniques, underscoring their potential in environmentally sustainable and scalable catalysis for the production of sustainable e-fuels.

In our method [BmIm][BF4] was employed as solvent with either $Fe(acac)_3$ or $Ru_3(CO)_{12}$ at 523 K for 18 hours. For bimetallic Fe-Ru NPs, three molar ratios (1:1, 3:1, and 9:1) were explored. These nanocatalysts were supported on γ-Al_2O_3 with variable metal loadings (1 or 4 wt.%). Characterization included XRF, XRD, SEM, and H_2 chemisorption analyses. Kinetic experiments were conducted at 593 K and 6 or 20 bar pressures, with adjustments to uphold CO_2 conversion below 5%. FT-IR gas analysis assessed yield and selectivity.

Our study showcases the heightened cooperativity of bimetallic Fe and Ru species synthesized via the IL method, yielding superior activity and selectivity for LPG-range hydrocarbons over traditional colloidal synthesis.

This study introduces an innovative method for synthesizing bimetallic 1% Fe-Ru catalysts using ionic liquids as solvents. Both mono(Fe)- and bimetallic catalysts Fe-Ru, prepared via the new method, demonstrate 12% higher selectivity towards C2–C5 hydrocarbons at 20 bar pressure, 5400 mL/h/gcat, and 320°C, where the main product obsewrved is CH_4, in contrast to the colloidal method catalysts with the same Fe:Ru ratio, which showed prominent selectivity to CO. For some catalysts, the selectivity to HC increases with lower space velocity from 0 to 15 %. Increasing metal loading to 4 wt.% in the Fe-Ru 1:1 IL catalyst significantly boosts C2–C5 hydrocarbon generation to 13 %. The selectivity shift from CO to methane and HC observed with IL-synthesized catalysts should be attributed to the synergistic interplay between iron and ruthenium, as confirmed by H_2-TPR reduction profiles, and the formation of iron carbide active species for Ftsynthes in reaction conditions.

ACTIVATED CARBONS DERIVED FROM AGRIFOOD WASTE FOR HYDROGEN STORAGE

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Recently, there has been an increasing focus on hydrogen (H_2) as a potential sustainable energy carrier, prompting extensive research into hydrogen storage methods to address its utilization challenges. Among these, solid-state systems are regarded as the safest way to store H_2 and porous carbon materials have emerged as promising candidates as hydrogen absorbers due to their lightweight nature, high surface area, and microporous structure, making them particularly suitable for physisorption approaches.

This study focuses on activated carbons (ACs) produced from the pyrolysis of agrifood waste, from common cereals to locally sourced waste such as asparagus stems, melon, and orange peels. The aim is to investigate these materials for physisorption-based hydrogen storage in solid-state systems. The biomass residues undergo a two-step process: initial pyrolysis at moderate temperatures (650°C) to produce a carbonaceous material known as biochar, followed by chemical activation using KOH as the activating agent, in order to modify the morphology of the materials, particularly in the development of microporosity. Analyses of specific surface area, pore characteristics, and hydrogen adsorption/desorption behaviors offer insights into the influence of chemical treatment on the hydrogen storage efficacy of the various activated biochar samples.

Experimental results demonstrate that KOH-activated carbon can significantly enhance the specific surface area, increasing it from 337 m^2/g of the non-activated reference to over 3208 m^2/g. These materials reveal also a significant increase in hydrogen storage capacity after chemical activation treatment. The best results nearly show H2 uptakes of almost 5 wt% at 77K and 20 bar.

The research emphasizes the economic and sustainable benefits of repurposing agricultural residues in line with circular economy principles. In fact, these materials are prized for their abundance and the ease with which their properties can be tailored through straightforward chemical processing methods, thus contributing to the advancement of clean energy technologies.

FAST MICROWAVE-ASSISTED SYNTHESES FOR OLD AND NEW POSITIVE ELECTRODES IN CONVENTIONAL AND SOLID-STATE BATTERIES

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Even though $LiCrO_2$ and $NaCrO_2$ belong to the same family of O_3-type layered oxides and share the same transition metal, they have significantly different electrochemical properties. The latter is one of the most popular active materials as positive electrodes in Na-based all-solid-state batteries, since its working voltage matches fairly well with the stability window of a series of solid electrolytes. The former, however, has proven to be electrochemically inactive vs. Li. When Li is de-intercalated, the oxidized Cr(VI) moves towards tetrahedral sites in the Van der Waals gap. To prevent the Cr migration, it could be synthesized a mixed phase possessing both Li and Na as interslabs cations, with the Na increasing the O-O distance (i.e. less stable tetrahedral sites). Nonetheless, the large chemical stability of both $LiCrO_2$ and $NaCrO_2$ hampers the synthesis of such mixed phase following conventional, quasi-equilibrium processes. Indeed, the synthesis of both $LiCrO_2$ and $NaCrO_2$ requires 5 hours of heat treatment at 900°C in an inert atmosphere.

Conversely, solid-state microwave-assisted syntheses, provide a high heat transfer rate to the reacting powders, leading to the possible formation of metastable phases. This reduces the reaction time, from hours to seconds, making these processes more attractive from both economic and environmental point of view. In the present work, $LiCrO_2$ and $NaCrO_2$ have been obtained from a fast microwave-assisted reactions, after 120 seconds of treatment at 500°C, in an open crucible. Moreover, a new mixed Li_x-$Na_{1-x}CrO_2$ phase has been successfully synthesized, with different Li/Na ratios. The highest purity has been obtained for x=0.58, after 60 seconds of treatment at 620°C starting from the carbonates of each alkali metals and chromium(III) oxide.

P-XRD highlighted that the quaternary phase crystallizes in the R-3m space group, as the ternary oxides do, with a cell parameter along c-axis intermediate wrt these latter. No peaks owing to a superstructure demonstrate that Li and Na are mixed in each WdV gap, and they do not form alternate layers. The formation of $Li_{0.58}$-$Na_{0.42}CrO_2$ has been followed by in situ synchrotron P-XRD simulating the fast-heating rate with a tuned hot blower, revealing an intermediate formation of a eutectic between the two carbonates.

Galvanostatic cycling tests show that microwave-assisted $NaCrO_2$ has the same electrochemical behaviour in both liquid- and solid-state cells of the same compound obtained via conventional synthesis, while the $Li_xNa_{1-x}CrO_2$ still shows poor to no activity vs. Li.

DLP OF TEXTURED ALUMINA CERAMICS: POWDERS SYNTHESIS, 3D PRINTING AND MICROSTRUCTURAL CHARACTERIZATION

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Natural materials with textured microstructures, such as nacre, bone and bamboo, have excellent mechanical performances, significantly higher than their corresponding materials (e.g. aragonite for nacre). Analogously, textured ceramics have attracted widely interest for applications in structural and functional ceramics thanks to their superior properties compared with ceramics composed of randomly oriented grains. Indeed, the incorporation of oriented grains favours several toughening mechanisms such as crack deflection, crack bridging and grain pull-out. In parallel, 3D printing can overcome traditional ceramics shaping limitations, such as reduced design freedom and post-production machining, and further promote the use of technical ceramics. Therefore, the design freedom conferred by 3D printing and peculiar properties of textured ceramics can be merged for the development of novel ceramics with functionalities and applications never investigated before.

First, different formulations containing alumina platelets, -alumina submicrometric powder and alumina precursors were investigated to determine optimal synthesis parameters. Then, the obtained powder was used to prepare photocurable slurries mixing the ceramic powder with a commercial photocurable resin. Slurries were optimised in terms of solid loading and dispersant amount, to accomplish viscosity and printability parameters. Finally, 3D printed samples were obtained using a Digital Light Processing (DLP) 3D printer. Samples were then sintered at 1600 °C to investigate physical and microstructural properties.

Geometrical density, after sintering 3h at 1600°C, of 3D printed samples without alumina precursors was significantly lower compared to the corresponding samples (a mixture of 50 vol% of alumina powder and 50 vol% of alumina platelets) containing alumina precursors, i.e. 65%TD and 78%TD, respectively. In both cases, an orientation factor, determined via XRD analysis, higher than 90% was achieved. For comparison, pressed pellets were prepared as well, and their orientation factor was approx. 40%.

The gel-combustion synthesis was effective in the deposition of alumina nano and micro-particles on the starting alumina platelets, improving sinterability and achieving higher densities compared to the corresponding formulation without alumina precursors. Interestingly, a strong anisotropic behaviour was observed for the shrinkage in the three directions (between approx. four and five times in the printing direction compared to the in plane one). Thanks to the involved shear rates during the printing process, a successful degree of texturing was obtained, as determined via XRD analysis and FESEM observations. In the next months, mechanical properties (flexural strength and fracture toughness) and other sintering conditions will be tested.

CORROSION RESISTANT PEO COATING ON ALUMINIUM 2024 WITH A BIOMIMETIC SURFACE FOR AERONAUTICAL APPLICATIONS

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The goal of this research is twofold: i) to mimic the scales (the so-called "riblets") of the mako shark skin on aluminium 2024 for aeronautical application in order to reduce the fluid-dynamic surface drag; ii) to improve the corrosion resistance by optimization of the plasma electrolytic oxidation (PEO) process.

After the definition of the proper bio-inspired texture (shape and geometry of the riblets), preliminary tests of PEO were carried out on aluminium alloy 2024. The effect of PEO process parameters, namely the electrical signal and the electrolyte composition, on plasma formation and on the properties of the oxide has been investigated. Microstructural analyses and electrochemical tests were carried out after PEO treatment.

Fluid-dynamic considerations suggest that the riblets profile does not play a major role in surface fluid drag reduction. Instead, the main parameters to be accounted are riblets spacing, length and tip radius. Among the different PEO parameters, an electrical signal consisting of a cycle 60% anodic and 40% cathodic, with a cathodic peak of 7% with respect to the applied anodic voltage (up to 400 V) seems to be the most promising in order to obtain a compact oxide. Moreover, the addition of glycerin to the silicate alkaline solution increases plasma stability.

Considering as possible applications a civil airplane and the hull of a racing boat, the width of the riblet is in the order of 50 and 10 µm, respectively. During PEO, a minimum potential of 300 V is required for triggering the plasma discharges upon the alloy. Moreover, the use of an a.c. voltage ramp to reach the highest voltage in following steps allows to obtain a high-quality coating. The results presented in this work are part of the research project "MAKO - biomimetic corrosion resistant aluminium for aeronautics", funded by European Union – Next Generation EU, PNRR - Missione 4 "Istruzione e Ricerca" - Componente C2 Investimento 1.1, D.D. n. 104/2022 "Bando PRIN 2022".

THROUGH-MASK ELECTROCHEMICAL ETCHING ON AA2024 FOR FLUID-DRAG REDUCTION

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Aluminum alloy 2024, featuring copper as its principal alloying constituent, stands as a prevalent choice in aeronautical and aerospace endeavors. In these fields of applications, polymeric adhesives incorporating a riblet-based microstructure, or components generated through additive manufacturing have been suggested to enhance tribological performance. The objective of this project is to develop a texture on oxidized aluminum surfaces to diminish drag force and enhance fluid-dynamic performance. Drawing inspiration from the riblets found on the skin of the mako shark, capable of achieving swim speeds of up to 75 km/h, the aim is to replicate these structures on aluminum surfaces for aeronautical applications. This texturing approach seeks to optimize fluid-dynamic characteristics by introducing similar microstructures onto the surface of aluminum components.

The surface of the AA2024 T3 aluminum alloy was subjected to electrochemical etching following the deposition of a pattern of parallel lines of varying thicknesses and spacings of a UV-curable dielectric-acrylic ink using the Ceradrop F-series ink-jet printer. Subsequently, by applying an anodic potential to the exposed metal surface immersed in a sodium nitrate solution (100 g/L), the material was selectively removed, thus creating the desired profile. Various potentials and currents were tested and correlated with the resulting surface.

The ink-jet technology enabled the deposition of a pattern of lines with a width of 100 microns, resulting in profiles with closely spaced riblets up to 130 microns peak-to-peak after etching. Optimization of the electrochemical parameters led to the determination of the best anodic current density and treatment time to achieve the ideal shape suggested by fluid dynamics simulations.

Achieving the ideal geometry faced several technological limitations at various stages of the process. The spatial resolution of the printing, in terms of the minimum achievable width of a single line, sets a limit on the final spacing of the riblets, which must in any case be greater than this value. The spacing of the pattern-mask must ensure a residual portion of aluminum not covered by the dielectric material to be activated electrochemically. The results presented in this work are part of the research project "MAKO - biomimetic corrosion resistant aluminium for aeronautics", funded by European Union – Next Generation EU, PNRR - Missione 4 "Istruzione e Ricerca" - Componente C2 Investimento 1.1, D.D. n. 104/2022 "Bando PRIN 2022".

PREPARATION AND CHARACTERIZATION OF BIOPOLYMER-BASED COMPOSITES WITH NATURAL FILLERS

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The urgency to find sustainable replacements for conventional plastics used in food packaging has recently drawn the attention of scientific research. Several natural materials, byproducts of food processing and agro-industrial processes, are employed as fillers to reinforce biopolymers, as sustainable alternatives to some of the petroleum-based plastics already in use. Mechanical behavior and barrier properties of the material, crucial features for packaging applications, are altered by the fillers. Moreover, the processing parameters may be influenced, thus impacting the overall sustainability of the product. Inulins, naturally occurring polysaccharides extracted from vegetables like chicory, are employed as fillers to produce poly(butylene adipate-co-terephthalate) (PBAT) composites, suitable for food packaging applications.

Different commercial inulins, having different chain lengths, were considered. PBAT-inulins (5 - 10 wt%) compositions were evaluated using a two-level factorial design and ANOVA for data evaluation. PBAT-inulins blends were processed with twin screw extrusion and injection molding to obtain dumbbell specimens (model 5A, according to ISO 527-2:2012) for tensile testing. The produced specimens were also characterized in terms of thermal and physico-chemical properties, to determine the effect of the fillers.

The processing of the blends was successful, and results will be presented concerning the characterization of the obtained composite materials. The specimens containing inulin proved to be stiffer than pure PBAT and with a reduced elongation at break.

The stiffness increase is a direct effect of the addition of inulin particles in the PBAT bulk. Deeper investigation of the inulin chains, and the particles' shape, dimensions, and interaction with the polymer matrix may promote a better understanding of the potential use of these materials for food packaging applications.

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PROCESSABILITY AND FILM PROPERTIES OF POLY(BUTYLENESUCCINATE)/POLY(LACTIDE) BLENDS SUBJECTED TO REPEATED EXTRUSION CYCLES

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To fully develop the potential of biodegradable plastics in terms of eco-sustainability, it is very important to correctly manage their end-of-life, too. In this regard, several studied have examined the environmental burden of different waste management options for both synthetic and biodegradable plastics, and mechanical recycling resulted to be the best choice.

In this work, the effects of repeated extrusion steps on the structure and properties of polybutylene succinate (PBS), polylactic acid (PLA) and their blends were studied.

The experimental plan of this study involved, first of all, the characterization of the neat PBS and PLA resins and the preparation of PBS/PLA blends at different weight ratios of the two polymers (a PBS-rich blend, with 80% of PBS, a PLA-rich, with 80% of PLA and a blend with 50% of both the resins). The materials were then subjected to five extrusion cycles and, at the end of each processing step, melt flow index and dynamic rheological measurements were carried out. For both the neat polymers and their blends, the pellets obtained after the first, third and fifth extrusion cycle, were processed by means of a laboratory-scale film blowing apparatus. Finally, these films were characterized in terms of mechanical, barrier, optical and thermal properties.

By increasing the number of extrusion cycles:

- the neat PBS and the PBS-rich blend undergo a re-gradation/branching process.
- The neat PLA and PLA-rich blend show a decrease in the polymer average molecular weight, due to thermo-mechanical degradation phenomena.
- For the PBS50/PLA50 blend degradation phenomena prevail, but their effect on the melt behavior is significantly less pronounced compared to the neat PLA.

The neat PBS and PBS-rich blend exhibit an excellent processability by film blowing, up to the V extrusion cycle, conversely to PLA and PLA–rich blend. The PBS50/PLA50 films can be successful produced up to the III extrusion cycle. Up to the V extrusion cycle, PBS-rich films retain mechanical performances suitable for general applications in food packaging. The PBS50/PLA50 film, after the III extrusion cycle, retains the mechanical properties of the virgin PLA. All the films exhibit transparency and color characteristics suitable for food packaging applications. In brief, this study assesses the thermo-mechanical recyclability of the neat PBS and PBS/PLA blends (specifically at 50 and 80 wt% of PBS), for which it represents a sustainable and complementary end-of-life option to biodegradability.

SILICA FROM WASTE OF FLUORINE-DERIVATIVES INDUSTRY APPLIED FOR MICROSCAFS® SYNTHESIS

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In the ambit of recovery of end-of-life products, silica has proven to be an example of effective waste valorization with a view to the circular economy. The aim of the present work is to investigate industry relevant applications of silicon dioxide derived as secondary product from the conversion process of hexafluorosilicic acid (H_2SiF_6 or FSA), a dangerous by product of fluorine and phosphate industry, into synthetic calcium fluoride. In particular, the silica obtained FSA, with controlled features and morphology is used in the synthesis of microspheres 40-80 μm), with interconnected microporosity MICROSCAFS®), replacing the conventional silica precursor tetraethyl orthosilicate (TEOS). The materials obtained were thus characterized and studied as photocatalysts for solar light driven photocatalytic degradation of organic pollutants in aqueous solution.

Silica is first recovered in gel form from FSA through a reaction with ammonia solution (pH of 8.5) at room temperature. The silica is then filtered, washed, and redispersed in deionized water, forming an FSA-silica dispersion, before the MICROSCAFS® preparation. Their synthesis technique combines polymerization-induced phase separation and sol-gel chemistry to form micro-sized spheres with tailored size and porosity. The FSA-silica dispersion is added to a hydrolyzed solution of (3-glycidyloxypropyl)trimethoxysilane (GPTMS), while a solution of glacial acetic acid and titanium(IV) isopropoxide (TiPOT) is prepared separately. These solutions are then combined and added to a water-in-oil emulsion, with decalin and Span 80 as oil phase, and vigorously stirred at 50°C. Ammonia is added at the final step, and the polycondensation reaction is allowed to proceed at 50°C for 30 minutes. The resulting MICROSCAFS® are separated by filtration, washed, dried, and appropriately heat-treated (550-900°C). Morphology and porous structure are assessed using Hg porosimetry, N_2 physisorption, and SEM analysis. The photocatalytic performance of the prepared materials was evaluated in a batch reactor for degrading two pollutants in water: an organic dye, methyl orange, and a widely studied broad-spectrum antibiotic, minocycline. Recovery experiments were conducted, showing material reusability and recyclability. The results were compared with samples obtained from conventional precursors, showing a correlation between material composition, surface properties, and photocatalytic activity.

The results indicate that the materials prepared with FSA-derived silica show promising results for this application, allowing to consider FSA as a valuable alternative to traditional precursors, especially for applications of high technological interest. Furthermore, the possibility of introducing titanium centers into media should be considered as a practical approach to prepare photoactive composite materials.

A NANOMECHANICAL APPROACH FOR EFFICIENT SUBSTITUTION OF COBALT IN HIGH-ENTROPY ALLOYS AND HARDMETALS FOR THERMAL SPRAYED COATINGS

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In the push for sustainable manufacturing, substituting Cobalt in "High entropy" alloys is critical. Promising Cobalt alternatives are multiprincipal alloys containing Al, that are based on abundant, affordability and eco-friendly elements. Within the CoBRAIN project, this strategy aims to transform European Manufacturing by developing thermal sprayed High Entropy Hardmetal coatings, that promise improved wear and corrosion resistance and ensure cost efficiency and environmental sustainability.

This study utilized High-Velocity-Oxygen-Fuel thermal spray coatings on AISI304 substrates. Feedstock powders, produced by MBN-Nanomaterialia(Italy), included an equiatomic "Cantor"-(CrMnFeCoNi) alloy, a hardmetal where 60 vol% TiC particles of ≤1 µm in size were added to the "Cantor" alloy, to improve wear resistance, and Cobalt-free high-entropy alloys and hardmetals with composition including aluminum in variable atomic percentage ($Al_x(Cr_{20}Fe_{40}Mn_{25}Ni_{15})_{100-x}$, with x = 0, 10, 14), to study its effect on coating performance. The mechanical properties were assessed using high-speed nanoindentation conducting 200x280 indentations for TiC-containing Hardmetal and approximately 90x90 for those without TiC, at penetration depths of 85 nm and around 240 nm, respectively. To analyze the nanoindentation data, statistical deconvolution was applied using Gaussian Mixture Models (GMM) and 2D GMM clustering to maintain the spatial distribution of the phases identified by this advanced approach.

Three mechanical phases were identified across the Al-containing samples without TiC: FCC (hardness 5.9±0.4 GPa), BCC (hardness 7.9±0.5 GPa), and Oxides (hardness 11±0.3 GPa). The hardness values of the phases remained comparable. Alloys without Al did not exhibit a BCC phase. In alloys containing TiC, the carbide content and hardness remained consistent among the different metal matrix compositions. The in-situ fracture toughness of the carbides, assessed through pillar-splitting tests, was comparable to the bulk properties of carbides, showing a value of $2.957 \pm 1.249 \mathrm{MPa}\sqrt{m}$. The high variance in fracture toughness values highlighted the coatings' intrinsic heterogeneity, with a bimodal distribution indicating two distinct types of carbides.

This study highlights the intricate relationship between material composition, microstructure, and mechanical properties in wear resistant coatings. The performance consistency in TiC-containing alloys, regardless of the cobalt substitution, suggests that the primary wear resistance mechanisms are preserved, with an enhanced contribution from the BCC phase: this underscores the potential of Al-containing multiprincipal alloys as a performance-enhancing alternative. The application of advanced statistical analysis for phase identification through deconvolution methods, alongside high-speed nanoindentation for mechanical property mapping, offers a comprehensive understanding of the coatings' behaviour.

ANALYSIS OF THE MICROSTRUCTURE AND DEFECTS IN INCONEL 738 SUPERALLOY MADE BY ELECTRON BEAM POWDER BED FUSION (EB-PBF)

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The current work deals with the processability and phase identification of a Ni-based superalloy rich in γ' phase processed by Electron Beam Powder Bed Fusion (EB-PBF). The superalloy discussed is Inconel 738 (IN738), which has excellent oxidation behavior and mechanical properties up to 1000°C. Due to the presence of γ' phase, IN738 is considered a hard weldable superalloy, increasing the challenge for its processability through additive manufacturing (AM). The use of an AM hot process, such as EB-PBF, with a specific alloy behavior simulation represents a valuable direction to overcome cracks formation during the building step.

IN738 powder (45-105 μm) was processed using an ARCAM A2X with standard process parameters. Residual porosity and general microstructure were evaluated, and the phase identification was performed using a simulated ThermoCal equilibrium diagram for IN738 alloy. Cracks were deeply investigated in terms of distribution, dimension, and neighborhood microstructural features to identify their formation mechanism.

The IN738 samples showed mainly spherical voids with a good level of residual porosity (<0.2%). The microstructure consisted of columnar grains elongated to the building direction with a size reduction towards the external edges of the samples. At high magnification, the γ' phase was identified inside grains coupled with carbides (MC and M23C6) along the grain boundaries. Cracks were mainly located in the top part of the sample following the grain boundaries. Severe chemical element segregations, MC, and M23C6 carbide precipitation were detected along the crack's line.

The presence of cracks stressed the need for a deep re-optimization of the preheating parameters and their impact on the melting ones. The segregation and carbide precipitation observed along the crack's path allowed the identification of the hot crack mechanisms in the investigated samples. In particular, M23C6 carbides were found to be active in promoting interfacial rupture in the Heat-Affected Zone (HAZ). This scenario can be correlated with the EB-PBF process when the solidified layer undergoes an increase in temperature due to the melting of the above ones, provoking cracks. The presented work underlined the crack mechanism that occurred during the EB-PBF building process of IN738. Moreover, it estimated that a proper EB-PBF parameter tailoring meant to reduce the M23C6 could allow the realization of crack-free IN738.

DENSE EUTECTIC CERAMIC OXIDE BY ADDITIVE MANUFACTORING: SUSTAINABLE BY-DESIGN MATERIALS AND TECHNOLOGIES (ECOBAM project)

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This project, funded by European Union – Next Generation EU, consisting in finding new solutions for the production of Al_2O_3-based directionally solidified eutectic systems by Additive Manufacturing. Al_2O_3 based directionally solidified eutectics ceramics have attracted a great deal of interest over recent decades due to their superior high-temperature strength retention and creep resistance to metal alloys, and higher oxidation resistance and microstructural stability, as compared with other ceramics. For these reasons they have been considered the most promising candidates for ultra-high temperature structural applications.

From the point of view of processing, oxide eutectic composite ceramics have been produced by several solidification methods which, however, cannot be used to obtain fine microstructure, large or complex shaped items. To overcome these shortcomings, additive manufacturing (AM) can be a very promising method to prepare monolithic and complex-shaped ceramic parts with fine and homogeneous microstructures. In particular Laser Power Bed Fusion (LPBF) and Direct Energy Deposition (DED) are AM technologies potentially suitable for directly shaping and sintering advanced ceramics in a single-step. This project aims to verify the applicability of these technologies to the production of Al_2O_3 based eutectics ceramics.

In order to realize innovative eutectic ceramic matrix composites with a refined interpenetrating microstructure and good mechanical properties, optimization of eutectic system properties (morphology, particle size distribution, flowability) and printing parameters have been performed. The study focused on evaluating the printability of the eutectic Al_2O_3-ZrO_2 composition using zirconia stabilised with 8 and 16 wt% of Y_2O_3. The addition of graphite to the studied compositions made it possible to evaluate its effect in the absorption of the laser beam.

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THE ROLE OF ANTISITE DEFECTS ON EXCHANGE BIAS IN DOUBLE PEROVSKITES

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Magnetic double perovskite oxides represent an important class of strongly correlated systems, exhibiting a large variety of multifunctional properties including multiferroicity, magnetoelectric coupling, magnetoresistance, magnetocaloric effect, half-metallicity, and exchange bias. To efficiently harness this huge potential in modern-day technological applications, it is necessary to gain a clear understanding of the relationship between the complex nanostructure and the exotic physical properties of these oxides. In particular, while the existence of antisite defects in DPs has been confirmed experimentally and via first principle calculations, their exact role in determining the magnetic behavior in these complex oxides is yet to be fully understood. In this work, we report a combined experimental and micromagnetic simulation exploration of polycrystalline Sm_2CoMnO_6, a prototypical double perovskite.

The sample was prepared via a conventional solid-state reaction method. The sample was structurally characterized using X-ray powder diffraction (XRPD), Scanning electron microscopy, and X-ray photoelectron spectroscopy. Magnetic measurements were performed using a physical property measurement system-based vibrating sample magnetometer from Quantum Design Inc. The micromagnetic model of the sample was developed with the GPU-accelerated software MuMax3.

The XRPD pattern reveals the presence of a single phase with a monoclinic structure (space group P21/n), as observed for bulk single crystals. The Rietveld refinement confirms crystalline domains of approximately 190 nm, agglomerated in larger polycrystalline grains of ≈1 μm, according to SEM observations. The magnetic characterization reveals a clear ferromagnetic order (TC about 140 K) with Magnetization vs Field curve exhibiting robust hysteresis with large magnetic anisotropy. The curve shows no sign of saturation even with an applied field of 9 T. The experimental data suggests a significant presence of antiferromagnetic antisite defects, however, no exchange bias is observed.

Despite the significant presence of antisite defects, our sample shows no signature of exchange bias, contrary to usual expectations in the case of antisite defects. This is explained by the micromagnetic simulations that confirm the presence of ferromagnetic nanoclusters and nanosized, random, and uncorrelated antiferromagnetic antisite defects, resulting in no exchange bias. This work provides a clear understanding of the role of antisite defects, in particular, on how their structure can lead to the presence/absence of exchange bias. The fundamental insight offered in this work fills an important knowledge gap in the field and will be of immense value in realizing the true potential of double perovskite oxides for future technological applications.

SUSTAINABLE SERICIN COATED NANOLIPIDS, AS TUNABLE PLATFORM FOR DRUG DELIVERY IN FOOD

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Nanotechnologies for drug delivery are extensively implemented in medicine, food industries, cosmetics, and environmental control, allowing high solubility, stability, and controlled release. Nanostructured Lipid Carriers (NLC) represent a development with self-assembling capabilities, providing high loading, exhibiting chemical and physical stability. A second Silk Sericin (SS) coating is applied to enhance mucoadhesive properties, ensuring stability and a controlled release during digestion. SS promotes cellular uptake and protects loaded compounds from enzymatic degradation. Vitamin A (VA), set as benchmark molecule for proof of concept, controls reproduction, embryonic development, eyesight and growth throughout various life stages. Due to its degradation upon exposition to light, high temperature and oxidation, the implementation of NLC-SS structures with long shelf life, cost-effectiveness, solvent-free nature, high biocompatibility, sustainability, and environmental friendliness is crucial. We designed and implemented a continuous detection method for VA loading, representing a significant advantage in food applications.

Food-grade status has obtained by using VA, lauric acid and Tween-80 dropcasted on water and subsequently coated with SS previously extracted from Bombyx mori cocoons. Protocols were optimized to minimize working temperatures (max 60°C) and to avoid excessive VA degradation. The obtained NLC-SS structures were characterized to evaluate stability and loading release capability by FTIR, DLS, ζ-potential, SEM, Raman, fluorometer, HPLC to investigate their structural and chemical properties.

NLC protocol demonstrated high reproducibility, a low energy consumption and a low working temperature. Loading efficiency was determined by fluorometer and HPLC, showing values depending on the different implemented coatings. Raman spectroscopy showed distinct chemical compositions in various layers, demonstrating the presence of VA within the structure, protected by the saturated lipids layer and the outer SS layer. Shelf-life stability was analyzed by DLS and fluorometer measurements, showing minimal variations (μm range) in average size over six months. Drug release was demonstrated by HPLC in digestion assays, illustrating the increased availability of VA in the small intestine where absorbed.

This study demonstrates the capabilities of NLC-SS to encapsulate the active ingredient through low-power consumption and food-grade processes using waste materials, avoiding a negative impact on the environment. NLC-SS ensures stability over time and a controlled release during the digestive process. The possibility of non-invasively monitoring the encapsulation efficiency during the production process gives an additional positive aspect to this technology. The ability to control the coating thickness to modulate resistance during digestion, makes this process suitable for applications for animal feed as well.

ELECTROSPUN MULTI-LAYERED STRUCTURES WITH ANTIFOULING PROPERTIES INDUCED BY SURFACE MORPHOLOGY

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Research into new antibacterial treatments to combat nosocomial infections is critical, given the significant impact of bacterial colonization on biomedical devices, leading to millions of infections annually. One promising approach involves creating surfaces with features unfavorable to bacterial adhesion that prevent colony formation and biofilm growth. Highly hydrophobic surfaces can deter biofouling through physical interactions, mimicking natural mechanisms. Our study proposes multi-layered electrospun structures with inherent antifouling properties based on the surface morphology.

Structures with superimposed layers of aligned fibers of poly(vinylidene fluoride-co-trifluoroethylene) P(VDF-TrFE) were electrospun and tested with Escherichia coli (E. coli). P(VDF-TrFE) 70:30 mol.% was dissolved in methyl ethyl ketone to obtain the solution, which was electrospun on aluminum or P(VDF-TrFE) film. Bacterial cultures were performed in Tryptone soy broth, tryptone soy agar and physiological solution. Morphological analysis of the fibers was performed by scanning electron microscopy. The method for fiber deposition, indicated as "n° layer-angle shift", consisted of rotating the sample by an angle (45°, 60° or 90°) after electrospinning each layer. Using this procedure, we fabricated structures with different fiber orientations. We report here the results of 4 layer-90° on aluminum (called 1st generation, 1G) and 10 layer-90° on P(VDF-TrFE) film (2G) structures. Static water Contact Angle was measured by the sessile drop method in air with a tensiometer.

The presence of a fibrous structure notably increased the hydrophobicity of the surface (contact angle equal to 127°± 5°, in contrast to that of the uncoated P(VDF-TrFE) film of 106° ± 2°). Water contact angle differed significantly between 1G and 2G structures. Although 1G structures partially restricted bacterial adhesion, the difference did not reach the level of significance compared to uncoated substrates. In 2G structures, featuring smaller pores than 1G, E. coli did not penetrate but adhered solely to the coating surface. 2G structures were effective in reducing E. coli adhesion in a statistically significant manner compared to uncoated P(VDF-TrFE) films by an average of 69%.

We fabricated multi-layered structures of electrospun P(VDF-TrFE) fibers, leveraging their surface morphology to achieve antifouling properties. These structures, consisting of up to 10 layers of fibers with a diameter of approximately 1 μm, were applied onto aluminum or P(VDF-TrFE) film with orientations ranging from 0° to 90°. The attainment of the Cassie-Baxter state was identified as crucial for enhancing the antifouling characteristics. Additionally, our findings underscored the significance of geometric features matching the size of the targeted bacteria.

CITRIC ACID DERIVED CARBON DOTS WITH ANTIOXIDANT ACTIVITY

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This study investigates the antioxidant properties of fluorecsent carbon dots derived from citric acid, demonstrating their longer activity compared to ascorbic acid.
Carbon dots were synthesized from citric acid via hydrothermal method. The antioxidant activity was evaluated using the DPPH assay, a common method for measuring antioxidant activity. The biocompatibility was evaluated through MTT assay in ovine fibroblast cell culture.
The results revealed that the citric acid-derived carbon dots exhibited significantly prolonged antioxidant activity compared to ascorbic acid and their non citotoxicity.
These carbon dots could be a promising candidate for applications where sustained antioxidant activity is required. Further studies are needed to elucidate the exact mechanisms behind the enhanced antioxidant activity and to explore potential applications in various fields such as biomedicine and environmental science.

HYDROGEN EVOLUTION REACTION (HER) PHOTOELECTROCATALYTIC ACTIVITY OF a-SnO_2/$SnSe_2$ HETEROSTRUCTURES

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Photoelectrocatalytic Hydrogen Evolution Reaction (PEC-HER) is a challenging way to produce green hydrogen by solar light harvesting. Specifically, 2D g-C_3N_4, 2D-GeSe, and 2D-SnSe have been successfully reported as promising interfaces for PEC-HER applications, considering their suitable band gap (in the range 1.5 – 2.5 eV), which perfectly matches the solar UV-Vis spectrum. In this work we investigated for the first time the PEC-HER properties of Liquid-phase exfoliated (LPE) 2D-$SnSe_2$ Metal Dichalcogenide (MD) interfaces in acidic media (pH = 0.5) and different UV-Vis lights. According to a controlled thermal annealing procedure of few layers 2D-$SnSe_2$, a-SnO_2/$SnSe_2$ heterostructure were formed, which increases the PEC-HER activity as respect to pristine 2D-$SnSe_2$ flakes. Amorphous/crystalline heterostructures represent promising interfaces for PEC-HER applications.
a-SnO_2/$SnSe_2$ heterostructures obtained by annealing at 250°C in static air LPE 2D-$SnSe_2$ commerical powders, have been spin-coated over Fluorine-doped Tin Oxide (FTO) conductive glass substrates and immersed in a pH = 0.5 (H_2SO_4 0.5 M in distilled water) electrolyte. The PEC-HER activity has been measured by Linear Sweep Voltammetry (LSV) by illuminating a-SnO_2/$SnSe_2$ heterostructures by monochromatic LED sources in the (320-650 nm) UV-Visible range.
Both as exfoliated 2D-$SnSe_2$ and a-SnO_2/$SnSe_2$ heterostructure exhibit maximum PEC-HER activity under 625 nm LED wavelength irradiation at 30 mW/cm^2, as respect to dark conditions. As a preliminary figure of merit, current densities at a potential of -0.8 V vs SHE increases from 0.036 mA/cm^2 (dark) to 0.107 mA/cm^2 (625 nm light) for the as-exfoliated 2D-$SnSe_2$ and from 0.010 mA/cm^2 (dark) to 0.117 mA/cm^2 (625 nm light) for the a-SnO_2/$SnSe_2$ heterostructure.
The photoelectrocatalytic activity towards HER of 2D-$SnSe_2$ is shown for the first time with promising preliminary results. Moreover, the positive effect of illumination on the H_2 production is enhanced for the a-SnO_2/$SnSe_2$ heterostructure electrode as compared to the as exfoliated 2D-$SnSe_2$ electrode. Partially amorphized a-SnO_2/$SnSe_2$ heterostructure preserves all the surface to volume advantages of the initial 2D material, however enhancing their PEC activity for the hydrogen evolution reaction.

MESOSTRUCUTRED ALUMINOSILICATES FOR DIMETHYL ETHER PRODUCTION FROM CO_2: ROLE OF THE NATURE, STRENGTH, AND DENSITY OF THE ACID SITES

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Global warming, consequence of CO_2 emissions, is one of the most prominent problems on a global scale; for this reason, research is focusing on green fuels obtained by the reduction of captured CO_2 (e-fuels). One of the most promising ones is dimethyl ether (DME), that can be used to replace diesel fuel. DME is obtained from CO_2 through two subsequent reactions. The first one, promoted by Cu-based redox catalysts, is the reduction of CO_2 to methanol; the second one, promoted by solid acidic catalysts, is the dehydration of methanol to DME.

Three different mesostructured aluminosilicates (Al-MCM-41, Al-SBA-16, and Al-SBA-15) and a mesostructured alumina (γ-Al_2O_3) are here proposed as methanol dehydration catalysts to be used in physical mixture with a Cu-based redox catalyst (CZA) for the one-step DME synthesis from CO_2.

All the aluminosilicates were synthesized with a Si/Al ratio of 15 by different sol-gel approaches: classical sol-gel for Al-MCM-41, EISA (Evaporation-Induced Self-Assembly) for Al-SBA-16, and solvothermal sol-gel for Al-SBA-15. γ-Al_2O_3 was synthesized with an EISA approach. All mesostructured catalysts were characterized with XRD, TEM and nitrogen physisorption to determine their structural, morphological, and textural properties. Some systems were characterized by ^{27}Al- and ^{29}Si-SS-NMR. A particular focus was put on the characterization of the acid sites with NH_3-microcalorimetry and pyridine-FTIR. The catalysts were finally tested for CO_2-to-DME conversion in a bench-scale plant with a fixed-bed reactor, correlating their performances with their acidic properties.

The structural, morphological, and textural characterization evidences a hexagonal (P6mm) mesopore arrangement for all samples with the exception of Al-SBA-16, that shows a cubic (Im3m) arrangement. The characterization of the acid sites indicates that γ-Al_2O_3 only features Lewis sites, while all the aluminosilicates show both Lewis and Brønsted sites; it also points out that Lewis sites are stronger than Brønsted sites. Another important observation is that γ-Al_2O_3 shows the highest surface density of acid sites (number of sites as a function of the surface area); among the three aluminosilicates, the one with higher surface density of sites is Al-SBA-16.

The catalytic tests show that Al-SBA-16 is, among all catalysts, the one with the highest dehydration activity, followed by the other aluminosilicates and, last, by γ-Al_2O_3. These results evidence that Brønsted sites are more active towards methanol dehydration than Lewis sites, due to their nature and their moderate strength, and that the proximity of such sites (high surface density) promotes methanol dehydration.

MIXED MATRIX MEMBRANES FOR CO_2 TO HYDROCARBONS: THE SEPARATION STAGE IN THE DAM4CO2 PROJECT

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The huge emissions of CO_2 in the atmosphere are triggering a climate crisis that threaten future generations. Implementing carbon capture and utilization strategies is mandatory to contrast this trend. Such methodologies should have excellent efficiency and minimal carbon fingerprint to be suitable for the purpose. Membrane-based technologies offer an interesting playground in this context, as foreseen by the DAM4CO2 EIC-Pathfinder project. In DAM4CO2, mixed matrix membranes (MMMs) are under development to both separate CO_2 and subsequently photoreduce it to hydrocarbons. This contribution specifically focuses on the separation stage. CO2 separation from flue gas is performed on MMMs containing metal organic frameworks (MOFs) as fillers. Adopted MOFs are selected according to their composition (featuring Earth-abundant, noncritical elements) and facile synthesis. These are incorporated on polymer based MMMs. Either pure MOFs/polymers and MMMs are characterized, to emphasize the effect of compounding on the overall separative properties. Characterization ranges from the assessment of bare performances (e.g. CO_2 uptake, selectivity vs. N_2/H_2O...) to the understanding of the interaction mechanism of CO_2 with the various components of the MMM.
Preliminary characterization of first-generation MOFs and derived MMMs shows as a key factor determining separation properties is the homogeneity of the dispersion of the filler within the polymeric matrix (mostly dictated by the morphology), rather than a superior sorptive performance of the filler. Spectroscopic investigation of MOFs/MMMs are ongoing to determine if the compounding also affects the interaction mechanism of CO_2 with respect to the pure phases.
Since the key role of MOFs morphology on their compounding with polymeric matrices, the future synthetic efforts will point toward the modulation of crystallites size and shape. The most promising MMMs will be then scaled up to pilot scale for real conditions testing.

(Cu, Ni) CATALYSTS FOR ETHANOL DEHYDROGENATION: EFFECT OF SUPPORT AND SYNTHETIC ROUTE

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In light of global environmental problems, new innovative and environmentally friendly sources for energy production and transportation must be found. Among all the possibilities, H_2 is an emerging energy carrier, that is a side product of bioethanol dehydrogenation to acetaldehyde, being an important intermediate and one of the most important petrochemical products. Among studied active phases, Cu- has received increasing interest due to its low cost and more environmentally friendly than copper chromite catalysts, which is the conventional catalyst for this reaction. In the literature, it has been shown that the addition of Ni to nanoscale copper alloys increases the stability and the performance of the catalyst. The aim of this work is the study of bioethanol dehydrogenation on (Cu,Ni) catalysts as a function of preparation procedure and thermal treatment.
The (Ni,Cu)/Al_2O_3 catalysts were prepared by hydrothermal treatment (HT) and optimized liquid combustion synthesis (CS), maintaining a total metal loading of 7.5 wt.%. The prepared catalysts were characterized by XRD, FE-SEM, FT-IR, UV-vis-NIR, and BET. The catalytic performances were carried out in a laboratory scale plant in a quartz fixed bed tubular reactor with 2.4 (v/v)% ethanol and 0.05 g catalyst in the temperature range 423-773 K. The influence of possible catalyst pre-reduction was also investigated. The reactant products were analyzed by GC and GC-MS to evaluate bioethanol conversion and acetaldehyde yield and selectivity.
The Cu-based catalysts, Cu (CS), showed the highest catalytic performances in terms of acetaldehyde production (73% yield) at 573 K with a maximum selectivity of 91% without catalyst pre-reduction. Moreover, the catalysts pre-reduction led to an increase of the catalytic performances at lower temperature with both prepared bimetallic catalysts.
The presented results showed that the catalytic performances are strongly influenced by the catalyst preparation techniques, the support choice and suitable pretreatment effect.

STABILIZATION OF PHASE CHANGE MATERIALS FOR THE THERMAL MANAGEMENT OF PHOTOVOLTAIC CELLS

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Solar power is widely recognized as one of the most significant sources of renewable energy. The performance of the PV system depends on the power output from the module, which is related to cell characteristics and also on environmental conditions (cumulative solar radiation, cell temperature, operating temperature, wind velocity, natural or artificial shades on the panel, hail, lightning, snow, ice, air-mass, clouds, dirt on PV surface, the latitude of installation, module degradation). Si cells has a conversion efficiency of about 20% at 25°C; every 1°C rise in temperature results 0.45 % drop of the already low maximum efficiency.

Three different Phase Change Materials with a melting temperature in the range 50-60°C were used. The PCMs were shape stabilized using expanded graphite (EG), polyethylene and ethylene-propylene-diene-monomer rubber (EPDM). The materials were characterized by leaking tests, thermogravimetric analysis, differential scanning calorimetry. The thermal conductivity was also determined, and the thermal behavior of produced panels was verified through climatic chamber tests.

The results showed the beneficial effects of a shape stabilization with polyethylene (rigid panels) and with EPDM rubber (flexibility). The combination with expanded graphite was essential in order to keep the thermal conductivity to sufficiently high values necessary to allow a good heat exchange between the PCM and the photovoltaic panel. The results of climatic chamber tests showed the beneficial effect of the PCM in the temperature management with a dampening effect in the heat propagation to the cell.

The beneficial role of expanded graphite, combined with polyethylene for rigid panels and with EPDM for flexible ones, was verified through thermal conductivity and climatic chamber tests.

CERIUM-OXIDE BASED CATALYSTS FOR DIRECT SYNTHESIS OF DIMETHYL CARBONATE FROM CO_2 AND METHANOL

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Dimethyl carbonate (DMC) is a valuable eco-friendly compound, and its increasing demand is due to its various applications (polycarbonates, fuel and the lithium-ion battery industries). There are several synthetic pathways that are used for the production of DMC, but most of them involve toxic and dangerous substances, as reagents, catalysts, and by-products. For example, most of the industrial production of DMC still uses phosgene, a highly toxic chemical that can cause several health issues. In recent decades, research has been focused on developing more sustainable synthetic approaches that can replace the phosgene method. Currently the attention has been paid on the direct synthesis from methanol and CO_2, converting the latter from waste into fuel. However, this strategy still remains at laboratory level because of poor conversions and low yields of DMC, due to thermodynamic stability and kinetic inertness of CO_2. In order to overcome these drawbacks, new and efficient catalysts have been developed. Among all, Ce-based catalysts are particularly promising for their chemical stability, redox properties, and high catalytic activity.

Low porosity CeO_2 and Fe-doped CeO_2 were prepared through hydrothermal (nanorods) and sol-gel self-combustion (SC) synthesis, mesoporous CeO_2 was obtained with a surfactant-assisted precipitation method, and impregnation methods were used to obtain mesostructured nanocomposites (10%wt CeO_2@SBA-15). The as-obtained catalysts were characterized using PXRD, TEM, FTIR, Raman and N_2-physisorption. In some cases, XPS measurements were performed. The direct formation of DMC from methanol and CO_2 was carried out in a batch reactor by studying different parameters such as temperature, pressure, amount of catalyst, and volume of methanol. GC-FID was used to evaluate the DMC formation.

The various synthetic strategies led to the obtainment of ceria-based systems with different microstructures and textures. CeO_2 and particularly Fe-doped CeO_2 nanorods are the most promising ones from the catalytic point of view, mainly due to the peculiar morphology. The superior performance of the Fe-doped nanorods could be ascribed to the co-presence of the hematite phase and the creation of the ceria/hematite interface. The worse catalytic performance is observed for the SC sample doped with iron where a complete insertion of iron into the ceria structure was achieved. Mesoporous CeO_2 shows intermediate performances. The homogeneous dispersion of ceria on SBA-15 through proper impregnation strategies (CeO_2@SBA-15) resulted to be a promising approach to design efficient catalysts. The effect of dehydrating agents is under study.

MICRON-SCALE FRACTURE TOUGHNESS OF 3D-PRINTED ALD-COATED NANO-CERAMICS

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3D-printed micro- and nano-architected ceramic metamaterials exhibit remarkable strength and stiffness while maintaining lightweight properties. However, recent research has demonstrated the sensitivity of nanoceramics to crack propagation resistance, with a reduction of 20% in the average fracture toughness at high relative humidity levels (RH>60%) compared to low-humidity testing.

This study examines possibilities of reliability enhancement, using two-photon polymerization–direct laser writing (TPP-DLW) to create pyrolytic glassy carbon micro-pillars and uniform 2.5D structures, which were then encapsulated with Al_2O_3 thin films. These films, applied through Atomic Layer Deposition (ALD), were meticulously engineered to achieve a uniform thickness of 50 nm at different deposition temperatures (PE-ALD @ 200 °C, Thermal ALD @ 200 °C and 350 °C). The research focused on assessing these ALD-coated films' impact on the micro-pillars' fracture toughness, which had a diameter of 5.8 μm, under extreme RH scenarios, with less than 5% and more than 60% levels, coupled with localized FIB residual stress measurements. A simpler model using lithographically fabricated silica pillars, identical in diameter to the glassy carbon pillars, is explored to bolster the study's validity. This model helped isolate the specific effects of the ALD coating by eliminating variables associated with glassy carbon. Both the glassy carbon and silica systems were analyzed using cohesive element simulations to factor in residual stress from the ALD process and the splitting effect.

Compared to the pristine defective high-humidity tested ones (1.86 ± 0.3 MPa$\sqrt{m}$), the results show an increase in the fracture toughness of ALD-coated pillars and gain independence from the relative humidity conditions (2.38 ± 0.2 MPa$\sqrt{m}$ and 2.35 ± 0.2 MPa$\sqrt{m}$ for RH <5% and >60% respectively). Tensile residual stresses were found in the ALD coating as a function of the deposition temperature; the thermal ALD at 350 °C process has the lowest values (~200 MPa) while the thermal ALD at 200°C has the highest (~800 MPa).

Tensile residual stresses from the coating contribute to the crack nucleation and propagation processes, potentially explaining the reduced fracture toughness in uncoated pillars at low RH. Contrarily, simulations suggest that ALD coating's compressive stresses might induce a balancing tensile stress in the substrate, leading to early crack instability. This discrepancy is clarified through findings from the silica system, likely due to secondary cracking in the glassy carbon pillars.

TOWARDS THE USE OF CATALYSTS WITHOUT ACTIVATION STEP: A CU-CuO/ZnO/ZrO_2@SBA-15 NANOCATALYST FOR CO_2 TO GREEN METHANOL CONVERSION

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CO_2-to-fuels pathway 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. The research in this field is encouraged by the prospect to convert CO_2 through reaction with hydrogen produced by water electrolysis powered from renewable energy sources, in the so called "Power-to-X" technologies. In this context, this work aims at a novel impregnation sol gel autocombustion combined approach that, through a cheap thermal decomposition in air atmosphere, results in a high-performing Cu0/CuO based catalyst, already active without any pre treatment, for methanol synthesis by CO_2 hydrogenation.

This study focuses on an innovative nanocatalysts preparation of both copper/zinc oxide@SBA-15, and copper/zinc oxide/ zirconium oxide@SBA-15 systems via a novel combined strategy of impregnation-sol-gel autocombustion whose behaviour in methanol synthesis from carbon dioxide hydrogenation was investigated at 250°C and 3.0 MPa with the aim of correlating the catalyst's performance with its physico-chemical features. The behaviour of the catalysts supported on SBA-15 in the methanol synthesis from an H_2/CO_2 stream has been investigated in a fixed-bed stainless-steel reactor and compared with that of an unsupported copper/zinc oxide/ zirconium oxide catalyst.

As a result of a multi-approach characterisation technique, the innovative preparation method allows to confine the desired active phase within the mesoporous system of the SBA-15, obtaining it directly through a calcination in a static atmosphere of air. This phase remains stable in air atmosphere even after months from its preparation.

The catalytic results show that the supported catalyst without activation procedure exhibits the same, or even higher, methanol yield per unit mass of active phase (450 $mgCH_3OH\ h^{-1}\ g_{cat}^{-1}$) compared to that subjected to reduction treatment (376 $mgCH_3OH\ h^{-1}\ g_{cat}^{-1}$). The unexpected slight improvement for the non activated nanocatalyst compared to that reduced in hydrogen atmosphere has been discussed in terms of: (i) some differences in the textural/structural properties and ascribed to a reorganisation of the active phase occurring during the reduction process; (ii) methanol selectivity enhanced due to a decrease of the Cu/Zn surface molar ratio. Thanks to the encouraging results outlined here, the obtained catalyst received the international patent (US 11,446,641 B2).

UV-CURABLE BIOBASED ANTICORROSION COATINGS

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Nowadays, the epoxy resins are leading the market of the anticorrosive coating sectors due to their high mechanical properties and superior stability in corrosive environment. However, the majority of epoxy resins, currently in the market, derives from petroleum-based monomers, which induce environmental pollution and are dangerous to human health. Therefore, finding green alternative to the epoxy thermosets building block can be considered of high priority to move towards a more sustainable production. In this work, two different studies will be presented. In the first study, three vegetable oils differing from their initial insaturation content are epoxidized and UV-cured. While, in the second study, an aromatic biobased monomer is chosen to develop UV-curable nanocaly reinforced coating composites. Subsequently, their mechanical properties and their anticorrosion performances are evaluated and discussed.

Diglycidylether of vanillyl alcohol (DGEVA, SP-9S-5-005), epoxidized rose hip seed oils (ERHO-4.5 and ERHO-6) and epoxidized grapeseed oil (EGRP-5) were synthetized and provided by SPECIFIC POLYMERS (Castries, France) France), cationic photoinitiator triarylsulfonium hexafluoroantimonate salts, mixed 50 wt% in propylene carbonate were purchased from Sigma Aldrich (Milan, Italy). The coatings were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetric Analysis (DSC) Dynamic Thermal Mechanical Analysis (DMTA), pencil hardness, solvent rub resistance test, contact angle. The corrosion protection effectiveness was evaluated by electrochemical characterization.

The biobased curing efficiency of the vegetable oils and of the DGEVA containing different amount of nanoclay was investigated by FTIR and optimized. The epoxy group conversion of the vegetable oils was higher than the one obtained by DGEVA, therefore in this last case a post-curing treatment was necessary to reach a good crosslinking degree. The thermal and mechanical properties and anticorrosion performances of the coatings varied according to the epoxidation degree and to the amount/dispersion of nanoclay.

The study conducted on the three vegetable oils highlighted that both the mechanical properties and the anticorrosion performances can be linked to the initial epoxy content. While in the bioreinforced composites of DGEVA with nanoclay, the anticorrosion performances were hugely affected by the dispersion of the nanofiller inside the matrix.

PROCESSING OF PURE COPPER VIA LASER POWDER BED FUSION USING A GREEN LASER SOURCE

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Copper is used in a wide range of applications thanks to its unique set of properties such as good corrosion resistance, low chemical reactivity, and good machinability. In addition, thanks to the excellent electrical and thermal conductivity, it is the reference material for many functional applications such as heat exchanger and radiators. However, the design of these systems is quite complicated because they involve a complex structure, which is difficult to achieve using conventional processing techniques. The development of additive manufacturing (AM) can overcome the requirements of geometrical complexity imposed for such applications. In fact, these technologies allow to obtain complex parts with a high design freedom and high customization. However, the processing of copper through AM is particularly challenging due to its high reflectivity at the wavelength of infrared lasers used in most the commercial Laser Powder Bed Fusion (L-PBF) equipment, in addition to its high thermal conductivity which quickly carries the heat away from the melt pool. The present work aims to investigate the processing of pure Cu by using innovative L-PBF system equipped with a green laser.

Cubic samples of pure copper were manufactured by using a Print Green 150 L-PBF system equipped with a green laser with a wavelength of 515nm and a maximum laser power of 200W. A design of experiment approach was applied to determine the proper set of process parameters such as laser power, scanning speed and hatching distance to obtain as dense as possible parts. The effect of their variation on the microstructure was investigated. Moreover, a preliminary assessment of the mechanical properties of parts was performed.

A process parameter window in a range of Volumetric Energy Density from 150 to 300 J/mm^3 was investigated. The characterization of obtained samples in term of relative density revealed the most promising combinations of process parameters allowing to obtain high density material. The microstructure of optimized samples showed columnar grains with the typical grain growth parallel to the building direction.

The processing of pure copper by using L-PBF system equipped with green laser allows to obtain high density samples; in fact, copper shows a higher absorption coefficient at the wavelength of green laser radiation with respect to infrared one. The obtained preliminary results are very promising enabling improved performances of built parts.

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DESIGN OF ADVANCED SELF-HEALING MECHANISM IN FIBER REINFORCED COMPOSITE

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The self-healing capability, defined as the capacity to repair damages and fully or partially restore lost properties and functions, has been demonstrated in various polymer types, including thermoplastics, elastomers, and thermosets. Thermoplastic polymers exhibit healing by molecular re-entanglement processes across broken surfaces when heated above their melting temperature. In recent years, significant efforts have been dedicated to developing new healing systems for thermosetting polymers. This presentation focuses on the development of innovative self-healing materials capable of partially restoring their mechanical properties under conditions of prolonged periodic loading and unloading, typical of aerospace applications. Composite materials used in such applications often exhibit defects due to their original inhomogeneity, leading to micro-cracking and delamination at ply interfaces. Electrospinning was employed to deposit a thin polycaprolactone (PCL) layer on carbon fiber fabric, producing fiber-reinforced composites with self-healing capability. These hybrid reinforcements were used to develop novel structural composites with electro-activated self-healing properties, where PCL served as an intrinsic healing agent. Healing efficiency tests showed that the laminate with 10 wt% PCL content exhibited up to 31% healing efficiency. A subsequent study focused on carbon fiber-reinforced epoxy composites with self-healing action achieved through jet-spun cyclic olefin copolymer (COC) mesh directly deposited on carbon fiber plies. Healing efficiency tests demonstrated that the laminate with 8 wt% COC content reported a healing efficiency of 9.4%, attributed to poor adhesion between COC and EP matrix. Continuing advancements in this field are currently focused on the integration of cutting-edge 3D printing techniques and the deposition of highly accurate patterns of thermoplastic materials onto carbon fibers prior to the impregnation process. This forward looking approach aims to push the boundaries of material design and enhance the structural properties of composite materials used in various applications. The utilization of 3D printing technology enables the creation of intricate and customized patterns, ensuring a precise and controlled application of thermoplastic materials onto the carbon fiber matrix. This tailored deposition process holds the potential to optimize the distribution of thermoplastics, enhancing the overall performance and functionality of the resulting composite structures. The emphasis on precise deposition onto carbon fibers before the impregnation stage signifies a strategic approach to enhance the bonding between the thermoplastic layer and the carbon fiber matrix. This targeted application seeks to maximize the synergistic effects between the chosen thermoplastics and carbon fibers, ultimately resulting in a composite material with improved mechanical, thermal, and self-healing properties.

NANOPOROUS CRYSTALLINE POLYMER MATERIALS FOR CONTROLLED RELEASE: STRUCTURAL FEATURES AND APPLICATIONS

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Commercial available polymers as syndiotactic polystyrene (sPS) and poly-(2,6-dimethyl-1,4-phenylene)oxide (PPO) being amorphous or exhibiting nanoporous crystalline (NC) phases will be presented. NC phases can be loaded with suitable guest molecules, as for instance molecules presenting antimicrobial activity such as carvacrol, thymol, hexanal, salicylic acid, leading to formation of co-crystalline (CC) phases characterized by well-ordered spaced molecules inside the polymeric crystalline lattice. The formation of CC phases allows the preparation of polymeric materials with high content of "active" molecules that can be retained and/or released in a controlled way. Structural features and possibly useful applications of NC and CC phases of sPS and PPO will be presented.

sPS was supplied by Idemitsu. PPO was supplied by Sabic, FTIR spectra were obtained from a Vertex 70 Bruker spectrometer. WAXD patterns were collected by a D8 QUEST Bruker diffractometer.

Films and fibers of sPS exhibiting amorphous, NC or dense γ phases, loaded with relevant antimicrobial molecules as carvacrol, thymol, parabens, hexanal, hexanoic, benzoic, salicylic acid (SA) are prepared and characterized by WAXD and FTIR measurements. Formation of CC phases with of sPS with SA, as an example, a lipophilic hydroxybenzoic acid widely used to treat many skin disorders such as acne and psoriasis, allows the preparation of fibers with a high content of antibacterial guest, which is retained by the fiber even after long term immersion in water at room temperature as well as after repeated washing procedures at 65°C. Lower amounts of SA molecules can be also loaded in dense γ sPS fibers, but are quickly released since absorbed only in the amorphous phase. Moreover, a simple, ecofriendly, procedure leading to formation of CC and/or NC sPS phases is described. The procedure is particularly relevant because not only involves a direct formation of CC phase but also a simultaneous axial orientation of sPS fiber, with related improvement of mechanical behavior.

In this study we showed the possibility of tuning both loaded drug amount as well as drug release kinetics, by simply selecting suitable crystalline phases of a commercial thermoplastic polymer, making sPS fibers possibly useful for many applications. In particular, fibers with sPS/SA CC phases could be useful for preparation of textiles and fabrics, which require antimicrobial guest retention. Fibers with sPS γ form could be used for cosmeceutical and medical patches that, on the contrary, require antimicrobial guest release.

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HIERARCHICAL ZEOLITES PREPARED VIA TEMPLATE-ASSISTED DESILICATION HYDROTHERMAL METHOD FOR CATALYSTS AND ELECTROCATALYSTS PRODUCTION

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Zeolites are well-known for their use as catalysts and supports for metal-based catalysts. They exhibit large surface area and high mechanical and chemical stability, without leaching of the metal phase. However, micropores pose some limitations for reactants and products diffusivity. The secondary mesoporous network of hierarchical zeolites could be a solution since this peculiar texture enhances the mass transfer phenomena inside the pores, promoting the accessibility of the active sites.

Commercial NaY zeolite (CBV-100) was modified by acid wash followed by hydrothermal (150°C) desilication with NaOH in the presence of CTAB for different treatment times. Bimetallic zeolites (with two of Cu, Fe, and Ni) were prepared from conventional and hierarchical zeolites by ion-exchange. All materials were characterized by N_2 physisorption, X Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM). Bimetallic zeolites were tested for chemical and electrochemical oxidation of glycerol.

N_2 physisorption results showed that super-micropores and narrow mesopores (ca. 4 nm) are present after desilication in the hierarchical zeolites. XRD results demonstrate that the hierarchical zeolites are still crystalline faujasites, although with a lower degree of crystallinity. TEM micrographs showed the presence of large voids inside the hierarchical zeolites and revealed the effect of the treatment duration on the shape and dimension of the particles. The catalytic tests showed higher glycerol conversion and products yields with hierarchical bimetallic zeolites compared to the conventional zeolites with the same metal ions composition.

During the hydrothermal treatment the CTAB micelles diffuse inside the damaged micropore texture, promoting the formation of both super-micropores and mesopores. Treatment time between 6 and 12 h showed the best results in terms of mesopore development and structure reconstruction. The improved catalytic activity observed for bimetallic hierarchical zeolites compared to the conventional ones is attributed to the enhanced diffusivity.

CLEAVABLE BIO-EPOXY RESIN PRODUCTION PROCESS, FIBER RECOVERY AND THERMOPLASTIC DERIVED MATERIAL CHARACTERIZATION

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The present study detailed the composite fabrication and full recyclability of a particular biobased epoxy resin. The full recovery of the thermoset matrix was possible thanks to the patented cross-linking agents called Recyclamine® that incorporate amino-acid-cleavable groups that allow the cleavage of the crosslink points of the epoxy-cured network. Thanks to a nonaggressive treatment required to break this particular cross-linking, the fibers remained unchanged, thus maintaining the virgin properties. The recyclability yield of the composite was tested, through a specific chemical process, demonstrating the possibility of separating and recovering both the constituent fibers and resin from the composite panels. The resulting recycled thermoplastic epoxy material was characterized and then used to manufacture specimens by injection molding.

Beluga Whale is the biobased epoxy resin. Both resin and Recyclamine® Extra Slow Hardener were purchased from R*CONCEPT (Barcelona, Spain). The composite laminate was fabricated using vacuum-assisted resin transfer molding. Composite weighing 10 g was solubilized in 300 ml of 40% volume of acetic acid solution at 80°C for 2 h. As soon as the thermoset dissolved, the acetic solution was filtered to recover the dried fibers. The filtered solution was neutralized in an NaOH aqueous solution of 20M. Finally, the recycled thermoplastic was washed with distilled water and dried at 50°C for 24h. This process was repeated until enough thermoplastic was obtained to manufacture samples by injection molding.

SEM analysis was carried out to evaluate any potential damage and residual polymer on the fiber surface due to the not complete chemical recycling process. No visible effects were seen when compared with the virgin fabric. The recycled thermoplastic was characterized by DMA and DSC. The tanδ vs. temperature was measured at a frequency of 1 Hz, starting from 0°C up to 120°C. The results showed a single pick centered around 65°C (Tg) and a Tg about 58°C by DSC. Melting temperature (Tm) about 120°C; tensile modulus E=2,5 GPa; tensile strength σ=57 MPa.

The mild conditions of this chemical process guaranteed very little chemical damage on the fibers. Recycled thermoplastic possesses excellent mechanical properties and share some attributes similar to those of cross-linked epoxies. We are currently considering the possibility to manufacture thermoplastic composites using recycled thermoplastic. This innovative technology enables the production of thermoset matrix composite materials that can not only maintain the qualities of materials made with conventional resins but, more importantly, also be environmentally friendly.

CATALYTIC OXIDATIVE DEGRADATION OF HIGHLY HAZARDOUS CHEMICAL AND BIOLOGICAL CONTAMINANTS OVER SULFONIC ACID ION-EXCHANGE RESINS

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Heterogeneous catalysis opens promising paths towards an innovative approach to the mitigation of risks through the decontamination of highly hazardous chemical and biological contaminants. For this purpose, cation exchange resins with acid sulfonic groups are a cheap, versatile, and effective tool for the in situ degradation of chemical warfare agents (CWAs) and the inactivation of pathogenic viruses and/or bacteria, in terms of safety, environmental sustainability and costs Material and Methods The resins are first activated by contact with 30 wt.% aqueous H_2O_2 for 10 min, then filtered and dried, to give rise to the self-decontaminating materials featuring both oxidant and acid active sites. In particular, a styrene divinylbenzene copolymer, Amberlyst 15 Dry (4.7 meq/g sites by dry weight) showed remarkable capa bilities in the catalytic oxidative abatement of 2-(chloroethyl)ethyl sulfide (CEES), a CWA simulant of blistering sulfur mustard, and, in the inactivation of two bacteria, *E. coli* (Gram and *S. aureus* (Gram+), and Monkeypox virus (MPXV) a DNA virus.

The activated Amberlyst 15/H_2O_2 system featured excellent conversions of CEES (up to ca. 89% after 3 h), with the gradual formation of the corresponding sulfoxide CEESO and further reaction to sulfone CEESO 2. Likewise, the same activated resin led to a decrease of >4 log10 of the viral titre and a decrease of 9 and 5 orders of magnitude of *E. coli* and *S. aureus* viability, respectively. It is worth noting that these encouraging results were achieved over a unique catalytically active system, exploiting a synergistic effect between H_2O_2 and H^+ sites, by following the same straightforward experimental activation protocol for the degradation of contaminants of chemical, bacterial and/or viral nature.

MULTI-SCALE CHARACTERIZATION AND FABRICATION OF NANOCOMPOSITE CERAMICS WITH IMPROVED TOUGHNESS FOR BIOMEDICAL APPLICATIONS

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Engineering and controlling microstructures in advanced ceramics is crucial, as structural reliability significantly impacts their functionality. Recent studies indicate the potential to develop CeTZP nanocomposites with superior high strength and toughness suitable for biomedical implants if a complete understanding of the underlying toughening mechanisms is elucidated at the multi-scale.

This research employs a comprehensive nanomechanical characterization methodology to explore the relationship between microstructure and crack propagation in CeO2-stabilized zirconia ceramics, both 3D-printed and isostatic pressed. The study employs single-phase samples with 10 to 12 mol% ceria and multi-phase samples with 10.5 mol% ceria plus alumina or strontium aluminate nanoparticles sintered under specific thermal conditions. Micro-pillars of various diameters were created via Focused Ion Beam milling and tested utilizing different nanoindentation tips geometries to measure crack propagation resistance via pillar-splitting, supplemented by comparisons with 3D-printed analogs. Raman spectroscopy was used to detect early phase transformations prompted by gallium ion damage during pillar fabrication, while FIB also assessed the residual stresses introduced by these manufacturing processes.

The research, validated by high-speed nanoindentation, revealed that CeO_2-stabilized zirconia samples across 10 to 12 mol% ceria concentrations showed hardness values ranging from 12.12 ± 0.75 to 14.44 ± 0.47 GPa. Toughness improvements were notably size-dependent, escalating from 2.5 "to" 4 $MPa\sqrt{m}$ as the diameter of the pillars increased from 7 μm to 35 μm and the ceria content increases. Adding alumina nanoparticles elevated toughness from 2 "to" 3 $MPa\sqrt{m}$. Conversely, strontium aluminate nanoparticles yielded lesser toughening effects. Raman spectroscopy further supported these findings by identifying gallium damage-induced phase transformations, particularly in smaller pillars (smaller than 7 um)

The fracture toughness in ceria-stabilized zirconia is significantly influenced by the activation energy for phase transformation and crack deflection mechanisms, which are more pronounced in larger pillars. The hardness increment with increasing ceria content suggests a direct correlation to the enhanced stabilization of the tetragonal phase. The KIc versus indentation elastoplastic energy graph is pivotal, providing insight into the intrinsic fracture toughness and the additional toughness imparted by phase transformation in monophasic samples. Alumina nanoparticles enhance toughness by crack deflection and stress re-distribution at the crack tips. Conversely, strontium aluminate nanoparticles contribute less to toughening due to their high-aspect ratios. These findings highlight the nuanced interplay between microstructure, compositional factors, and mechanical properties, guiding the engineering of ceramics with optimized toughness.

VAT 3D PRINTING OF IONICALLY CONDUCTIVE POLYMERS FOR TACTILE SENSORS

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Smart sensors based on conductive soft polymers have shown remarkable potential whenever a link between the "soft" human world needs an interface with the "rigid" electronic one is required, in fields like wearables and soft robotics. However, conventional manufacturing technologies, such as casting processes, limit the obtainable shapes and applications.3D printing offers a valid alternative for producing customizable and conformable sensors and, among the printing technologies, light-induced ones allow high printing precision and fast production. Nevertheless, the development of highly deformable and conductive thermoset photocurable polymers is not trivial; merging these requirements to those linked to the 3D printability of the formulation makes the target challenging.

Different photocurable networks based on acrylated monomers and different crosslinkers/copolymers are here proposed. The formulations were doped with different salts to induce the ionic conductivity. The photopolymerization reaction was followed by photorheology before printing with a DLP apparatus with light source centered at 395 nm. The 3D printed samples were characterized in terms of mechanical properties combined with electrical measurements. Sensors' electromechanical performances were evaluated by means of tensile and compressive tests, using a universal testing machine while electrical impedance was measured in real-time by an LCR meter.

In a first study photocurable ionic conductive hydrogel based on a PVA- Polyacrylic acid semi-interpenetrated polymeric network, doped with NaCl, was synthesized and 3D printed in different complex shapes that can enhance the sensing properties. This material possessed exceptional mechanical behaviour, sensitivity and, furthermore, showed the capacity for self-repair. Alternatively, a mixture based on acrylic acid and hydrated ZnCl was used to homogeneously disperse cellulose pulp extracted from local waste. The dispersion procedure allows to partially solubilize and functionalize the cellulose obtaining a 3D printable formulation that allows the precise printing of highly stretchable and sensitive structures presenting stable response at different temperatures. Beside these, different materials based on innovative crosslinkers are currently under investigation.

POSTER

1st POSTER SESSION

RECYCLED POLYPROPYLENE WITH ENHANCED PROCESSABILITY: EFFECT OF A REPAIRING ADDITIVE

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Plastic recycling is a key aspect to achieve effective polymer circularity, especially for polyolefins for which usually the mechanical recycling is considered a downcycling process. The last, due to the progressive deterioration of the polymer microstructure during the reprocessing, leading to a gradual loss of processability and properties, hence compromising the added value of r-polyolefins. In this context, in this work the effects of the thermomechanical degradation and of the introduction of a commercially available repairing additive on the evolution of the polypropylene (PP) microstructure were evaluated, aiming at proposing an effective upcycling strategy for achieving recycled PP with enhanced processability.

The mechanical recycling of PP was simulated by subjecting the material up to 9 re-processing cycles using a twin-screw extruder. The repairing additive (Nexamite R201 (NEX), Nexam Chemical) was introduced at 5 wt.% within PP during the first reprocessing cycle of PP (to simulate pre-consumer recycling) and in PP already subjected to 8 reprocessing cycles, mimicking the typical conditions of a post-consumer recycling. The NEX-induced microstructural modifications of PP during the reprocessing cycles were monitored through rheological, thermal, and spectroscopic analyses.

Firstly, the microstructural changes induced by the thermomechanical degradation that PP undergoes during a typical mechanical recycling process were evaluated through rheological and thermal analyses. The obtained results confirmed that the main mechanism of degradation of PP involves the occurrence of chain scission reactions, resulting in a severe progressive decrease of the polymer molecular weight. FTIR analyses suggested that the structural degradation affecting the polymer molecular weight is predominant as compared to the functional degradation, since the oxidative degradation undergoes from PP is quite negligible. A detailed rheological study allowed demonstrating that the introduction of NEX can effectively prevent the decrease of the molecular weight of PP, especially when the additive is added in a low degraded PP (i.e. in the case of pre-consumer recycling). Furthermore, it was also showed that NEX can induce some melt structuring phenomena, involving the obtainment of branched structures or crosslink points, especially if the melt processing is carried out for long residence times. Finally, the results coming from DSC analyses confirmed the inferred modification of the PP macromolecular architecture.

INNOVATIVE POLYIMIDE-BASED MATERIALS WITH SELF-HEALING PROPERTIES FOR SPACE APPLICATIONS

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Self-healing polymers are smart materials that can heal their original structure and properties after mechanical, thermal, or radiation damage. Currently, polymer-based materials with self-healing properties are emerging in the aerospace field, where they can extend the useful life of structures, starting a self-repair at the onset of damage. Indeed, a spacecraft's surface can be damaged by impact with micrometeoroids and lunar dust, and this compromises the astronaut's safety and the success of the mission. Polyimides (PI) are polymers with suitable properties for space applications. PI-based materials possess high-temperature and chemical stability, outstanding mechanical properties, flexibility, and resistance to UV radiation, making them ideal candidates for the realization of structures in space environments.

Polyimides with self-healing properties were synthesized in a non-toxic bio-based solvent (dimethyl isosorbide) following a green synthesis approach that was recently developed by our group. During synthesis, selected additives were incorporated to enhance the intrinsic self-repair ability after mechanical damage. Samples were tested before and after mechanical damage to evaluate the self-repair properties. The thermal stability was evaluated by differential scanning calorimetry (DSC). An optical tensiometer was used to determine the surface hydrophobicity and surface free energy, whereas the mechanical properties were investigated by dynamic mechanical analysis (DMA).

In this work, a balance between the mechanical stiffness of the polyimides and their self-healing properties is pursued. In particular, we investigate an intrinsic and autonomous repair mechanism, which is based on either reversible supramolecular interactions or dynamic covalent bonding and is not triggered by external stimuli. Polyimides were synthesized in a two-step procedure using different concentrations of aromatic diamines and dianhydrides. The obtained poly(amic acids) were functionalized to achieve suitable self-healing properties and then imidized by heat treatment. The reversibility and dynamicity of the chemical bonds, which are crucial for self-healing, were analysed by FTIR spectroscopy. Results in terms of the degree of imidization, chemical structure, thermal stability, hydrophobicity level, and mechanical properties were used to assess the strength and durability of the polyimide-based materials in the space environment, as well as to evaluate their self-repair ability under mechanical damage.

CHARGE ORDERING AND MAGNETIC TRANSITIONS IN NANOSTRUCTURED $Ho_{0.5}Ca_{0.5}MnO_3$ MANGANITE

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The 3d based perovskite-structure materials containing rare earths are of recognized importance, owing to the development of new materials designed for different potential technological applications, such as ferroelectric thin films, microwaves, spintronics and semiconductor technologies. The half-doped perovskite $Ho_{0.5}Ca_{0.5}MnO_3$ presents a highly stable insulating AFM ground state. Ferroelectricity and its interconnections with antiferromagnetism have not been investigated anymore, outclassed in interest by the phenomenon of charge ordering common to all Ca^{2+} half-doped $RE_{1-x}Ca_xMnO_3$ manganites. We investigated the magnetic properties of samples of $Ho_{0.5}Ca_{0.5}MnO_3$ nanoparticles with different sizes in the nanometric range.

$Ho_{0.5}Ca_{0.5}MnO_3$ nanoparticles were prepared by a sol-gel self-combustion process followed by calcination. The samples have been prepared starting from the same batch, in order to obtain samples with the same composition which differ only in particle size. The X-ray powder diffraction patterns were collected on a Siemens θ-2θ D5000 diffractometer (Cu kα) equipped with a secondary beam graphite monochromator; data were refined by the Rietveld method by means of the software MAUD. The magnetic properties have been measured with the vibrating sample magnetometer of the Physical Properties Measuring System by Quantum Design, in the temperature range 2-380 K and in the magnetic field range 0-90 kOe.

The charge ordering and Neel's temperatures have been determined by zero field cooling and field cooling susceptibilities. By the field cooling susceptibility the effective numbers of Bohr's magnetons have been determined above and below the charge ordering transition; the ratio of the respective Curie's constants has been calculated. The parameters of the hysteresis cycle in the temperature range from 4 K to 300 K have been determined.

The value of the ratio of the Curie's constant above and below the first transition prove that it is a charge ordering transition. The antiferromagnetic interactions in the paramagnetic state give rise to the antiferromagnetically ordered state in the low temperature region. As it concerns this state, we investigated for possible differences in the magnetic order depending on the size of the particles; furthermore, we investigated for the presence of a glassy state.

3D PRINTING OF MULTIFUNCTIONAL MAGNETO-BASED NANOCOMPOSITES

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In recent years, the integration of nanotechnologies into 3D printing processes is unlocking unforeseen possibilities for the manufacturing of multifunctional devices that can be adapted to different application scenarios. Indeed, the synergetic incorporation of functional nanofillers within printable polymeric matrices offers the unique opportunity to design advanced nanocomposites (NCs) whose superior functionalities can be modulated in a multiscale approach. In this context, the integration of two different nanoparticles (NPs) into a photocurable polymeric matrix is here proposed as versatile method to enable the 3D printing of multifunctional NCs that can adapt to different application scenarios by means of digital light processing (DLP).

Poly(ethylene glycol) diacrylate was chosen as photocurable oligomer. Iron oxide (Fe_3O_4) and silver nitrate $AgNO_3$ were selected as magneto-responsive nanofiller and precursor of Ag NPs, respectively. A two-components radical photogenerating system (Bis(2,4,6-trimethylbenzoyl) phenylphosphineoxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one) was employed for the initiation of photopolymerization and the photoreduction of $AgNO_3$. Preliminary rheology investigations were performed to assess the DLP printability of the formulations. Hysteresis loop and two-point probe measurements were carried out to evaluate the magnetic and electric behavior of the NCs, while their antibacterial activity against different bacteria strains was investigated by disk diffusion method.

Magneto-responsive NCs displaying additional electrical and antibacterial properties were successfully fabricated by exposing a photocurable oligomer (PEGDA) embedding Fe_3O_4 NPs and $AgNO_3$, first to a DLP apparatus, and then to a UV-radiation, to induce the photogeneration of Ag NPs. The results showed that adjusting the composition of the photocurable formulations led to easily tailor the properties of the NCs. In particular, their magnetic response increases with increasing loading of Fe_3O_4 NPs, while their electrical conductivity and antibacterial activity increase by increasing the content of $AgNO_3$, as a result of a surface enrichment of Ag NPs generated during the UV post-processing.

This work explores a strategy to enable multifunctionalities in 3D printing processes via the integration of two functional nanofillers into a photocurable resin, namely Fe_3O_4 and Ag NPs.

This allowed to design remotely-controllable magneto-responsive NCs which offer huge potential for the fabrication of magneto-driven devices for both soft electronics and biomedical applications.

EXPLORING THE MECHANOCHEMICAL BEHAVIOR OF METAL CATALYSTS IN ORGANIC REACTIONS

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In materials science, the development of catalysts that combine efficiency and selectivity in chemical reactions is becoming increasingly important due to potential supply constraints of essential raw materials. This challenge places elemental metals in the spotlight. The role of mechanochemistry in organic synthesis further highlights the importance of efficient catalysts and prompts inquiry into how mechanically influenced surfaces interact with chemical environments. Preliminary findings suggest a possible enhancement in catalytic effectiveness with mechanical activation.

All the reagents and materials were purchased by Sigma Aldrich, TCI, Fluorochem and/or Chempur. The ball mill instruments used for this study were high-energy vibrating ball mills, equipped with 10 mL screw-type stainless-steel jars and one stainless-steel ball (Φ= 9 mm, 2.85 g). Electronic Microscope analyses are performed using a FEI Quanta 200 instrument (SEM). ^{1}H- and ^{13}C-NMR are collected with a Bruker Avance III HD 600.

A different response of the metals to repeated mechanical stimuli leads to a divergent selectivity towards the organic reactivity, akin to the variations observed under diverse chemical environments.

Our study investigates the effects of mechanical processing on the efficacy of elemental metals as catalysts in organic reactions. Utilizing benzophenone as a representative substrate, we demonstrate that the catalytic capabilities of such metals are influenced by various processing factors and conditions. The extent of this impact varies across different metals, as indicated by a series of characterization techniques and control experiments.

DEVELOPING MECHANOCHEMICAL TECHNOLOGIES TO RENDER CROP-PROTECTION AGROCHEMICALS GREENER (DEMETRA)

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Soil is the second largest natural carbon sink after oceans, significantly exceeding the capacity to capture carbon dioxide from the atmosphere of forests and other vegetation. At present, the soil is facing daunting challenges due to degradation, erosion, desertification, decline in organic matter, and biodiversity loss. Agriculture contributes significantly to these processes as well as to global warming. The Thematic Strategy for Soil Protection includes contamination from pesticides among the prominent soil threats in the EU. Developing green pesticides has become a stringent need. Under these circumstances, new synthetic routes to green agrochemicals are highly desirable. In this regard, mechanochemistry represents a promising solution.

DEMETRA intends precisely to design mechanochemical routes to novel green agrochemicals based on natural, or naturally derived, chemical substances through solid state-ionic exchange processes eventually forming hybrid materials carrying active molecules within lamellar solid and biochar matrices.

Sustainable mechanochemical methods to perform solid-state anionic exchange processes taking advantage of biochar and layered double hydroxides (LDHs), thus forming hybrid materials carrying active molecules in soils and controlling their release into the environment, have been considered. Analytical and numerical kinetic modeling of mechanically activated solid-state ionic exchange processes underlying the preparation of hybrid materials based on the use of biochar and LDHs, accompanied by a characterization of milling dynamics in utilized ball mills based on experimental and numerical simulation methods.

Biochar derived from biomass pyrolysis has been used as the matrix to host exchangeable cationic species. By mechanochemical action in the presence of quaternary phosphonium salt with antimicrobial activity, the biochar has been properly functionalized via cation exchange in a short time in dry conditions, providing a salt uptake of about 15 wt%.

The study has been focused first on Biochar used as the matrix to host exchangeable cationic species and a phosphonium quaternary salt as a reference cation. The hybrid material has been fabricated under solvent-free processing conditions by a mechanochemical approach optimizing the process by changing the milling time and the reagents ratio The resulting adduct was proven to enable the controlled release of cationic adducts.

HIGH-SPEED NANOINDENTATION MAPPING: ENHANCING MEASUREMENT RELIABILITY ON HETEROGENEOUS SOFT MATRIX MATERIALS VIA AN INNOVATIVE PILE-UP ERROR CORRECTION PROTOCOL

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Innovative nanoindentation techniques enable rapid mapping across large areas for advanced composite materials, assessing their complexity and establishing relationships between properties, microstructure, and performance with Machine Learning aid. However, errors often compromise accuracy, particularly pile-up effects on hardness and modulus measures. Traditionally, addressing these requires direct, time-intensive measurements of indentation contact areas, typically via ATM. This study introduces a quicker, efficient method to assess and correct pile-up by leveraging high-speed nanoindentation to alter surface roughness significantly, measured swiftly through optical profilometry. This approach confirms a direct correlation between the resultant surface roughness change and pile-up height, offering a fast alternative for evaluating nanoindentation effects.

Materials including 1 μm thick PVD films of gold, copper, titanium, and chromium, along with their bulk counterparts, were tested using high-speed nanoindentation at various depths (300 nm to 1000 nm) to generate different pile-up level. Fused quartz was additionally examined to validate the method, especially under sink-in dominated indentation. Pile-up height was quantified using AFM, while surface roughness changes, within and around the indent arrays, were assessed via confocal optical profilometry. This was conducted under two magnification levels (100X and 150X objectives). The approach was applied to Stellite alloys used in TBM high-wear resistant seals to adjust for pile-up effects in the cobalt matrix, ensuring the integrity of the mechanical properties of hard carbides.

The results show a linear correlation between the change in surface roughness and the nanoindentation depth. Moreover, a single linear calibration curve can be derived for the bulk materials and the coatings, evidencing how the pile-up height and surface roughness are proportionally related for each type of material system. The reported correction percentage due to pile-up in the material are for example 18% for titanium and 24% for copper. Finally, in the stellite sample the proposed approach was able to deconvolute piling-up phases (i.e. Cobalt) and correct its initial values (E = 255G Pa H = 6,5G Pa) modifying the mechanical response by a factor of 20%, while preserving the values for the carbides.

The obtained correlation functions could provide a direct basis, being provided the mapping of a family of calibration coefficients over different material properties and magnifications, to estimate pile-up height and consequently perform correction of the hardness and elastic modulus in a fast and reliable way, overcoming limitations imposed by AFM acquisitions and suggesting promising applications for fast in-line measurements within the advanced manufacturing industry.

INCREMENTAL FORMING OF NATURAL FIBRE REINFORCED POLYPROPYLENE COMPOSITES

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Incremental forming is an emerging materials processing technology that presents several peculiar characteristics like reduced tooling, cycle time and cost and ability to manufacture customized products. Originally proposed to shape metal sheets, its application was then extended to polymers and composite materials. Concerning the last ones, an area of great attention is the production of natural fibre reinforced polymer composites; natural fibres can replace synthetic fillers to increase some properties of the commercial synthetic polymers and further make them semi-biodegradable.

The simplest variant of incremental forming, known as single point incremental forming, was employed to manufacture cone frusta with a fixed wall angle, starting from natural long fibre (hemp and flax) reinforced polypropylene composites, obtained by a moulding process. The tests were carried out at room temperature using a high-speed four-axis vertical machining centre that drove the forming tool, a non-rotating stainless-steel stylus, in order to deform progressively the clamped composite sheet.

The experimental campaign aimed to evaluate the correlation between the wall angle and the height of the cone frusta when the failure occurred, as well as the type of failures and defects. In addition, it furnished information on the forming forces and the energies to carry out the manufacturing process.

The results highlighted reduced formability due to the nature of the reinforcement (long fibres). At the same time, the process can be used to obtain different shapes without using dedicated dies and with low levels of force and energy. A significant application can be the shaping of stiffening ribs for parts like panels in automotive, aviation and naval fields. Future research could provide for the investigation of the influence of other process parameters (like the shape of the forming tool of the toolpath strategy) on the formability limits of the natural fibre reinforced composites when formed incrementally, the numerical modelling of the forming process and the evaluation of the mechanical properties of remoulded panels after incremental forming.

DESIGN, DEPOSITION AND PERFORMANCE EVALUATION OF CONDUCTIVE INKS FOR WEARABLE ELECTRONICS

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This study focuses on the development of multifunctional electronic textiles, known as e-textiles, to improve safety, comfort and remote monitoring for people, workers and patients, especially in the biomedical field and occupational contexts. Smart fabrics offer a comfortable alternative by integrating wearable electrodes and sensors directly into the fabric to enhance functionality. Overcoming manufacturing challenges, this study presents an innovative, fully washable and flexible conductive fabric. By using commercial and specially designed inks with 1D and 2D carbon fillers, such as carbon nanotubes, graphene derivatives and silver nanowires, conductive ink stripes could be produced on different types of fabric with different resistivity values by screen printing.

Conductive ink deposition on three fabrics, i.e. knitted stretch cotton, 100% woven cotton and 100% woven polyester, was realised by screen printing using both GUP® C paste, (GrapheneUP, Czeck Rep) and innovative inks developed by dispersing conductive fillers in polymeric binders. A suitable TPU-based material was formulated and used as a washable protective coating. A morphological study to investigate the filler distribution was performed by SEM analysis (Quanta 200 FEG, FEI, The Netherlands). Resistivity tests were performed with a 4-probe multimeter to assess electrical conductivity. Finally, smart tissues were characterised both as thermal heaters and as electrical circuits to transmit physiological signals generated using a patient simulator (MedSim 300B).

The final properties of the smart textiles, such as electrical conductivity, electrical signal capability and thermal heating capability, depend on the type of substrate, as well as the ink formulations, the presence of conductive fillers and the weft direction of the fabric. Textiles with preferential warp and weft directions have lower resistivity and accurate signal acquisition. The presence of protective coatings, developed using water-based aliphatic thermoplastic polyurethane with various cross-linking agents, facilitates washing and drying tests without compromising electrical conductivity.

The results highlight that the performance of commercial deposited inks is interesting, the carbonaceous fillers are effective, but the commercial inks exhibit always superior performances, whereas polyurethane coatings allow long-lasting durability of inks, protecting them from the washing leaching due to washing cycles. The results show the potential of the developed materials for the production of smart wearable devices by screen printing and represent a significant step in the development of smart wearable devices integrating innovative materials and consolidated technologies.

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AN INNOVATIVE TWO-STEP ELECTROCHEMICAL PROCEDURE AIMED TO IMPROVE THE MECHANICAL PERFORMANCES AND THE CORROSION RESISTANCE OF FIBER METAL LAMINATES

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One of the main challenges in the aerospace industry is replacing chromic acid anodizing due to its health and environmental risks. This process ensures optimal corrosion resistance and mechanical strength in adhesive joints. In this study, tartaric-sulfuric acid (TSA) and sulfuric-phosphoric acid (PSA) anodization were combined, traditionally used separately, to create a two-step process. This aims to enhance both corrosion protection of metal substrates and their adhesion to fiber-reinforced polymer substrates, thus offering a promising solution to industry concerns.

Fiber metal laminates (FMLs) were made of anodized aluminium alloy 7075 and carbon fabric reinforced polyether ether ketone (PEEK). Metal substrate was first anodized in TSA for 10 min, 14V,37°C and then in PSA for 10 min,18V, 28°C(TSA-PSA). In this way, it was possible to obtain an anodic porous layer with small-diameter pores on the surface, which favour corrosion protection, and larger-diameter pores on the inside, which promote interlocking with the polymer matrix. The reverse order of the two steps was also performed (PSA-TSA) for the sake of comparison. Furthermore, TSA (20 min, 14 V, 37°C) and PSA (23 min, 18 V, 28°C) anodizing treatments were carried out separately, as well as a mechanical abrasion treatment with sandpapers (MT). Finally, a post immersion in a NaOH 0.1 M solution (TSA-NaOH) of only TSA samples was carried out to evaluate the effect of a pore-widening step on the anodic layer. Electrochemical impedance spectroscopy was performed to study the corrosion resistance of samples. The mechanical characterization of FMLs was conducted by evaluating their mode I fracture toughness and interlaminar shear strength (ILSS).

As expected, EIS tests showed that metal substrates anodized in TSA show the best corrosion resistance whereas the PSA ones the worst. The corrosion resistance of TSA-PSA samples is comparable to TSA, while PSA-TSA samples follow the PSA.As regards the mechanical properties, it was found that TSA-PSA and PSA samples are comparable: i.e., they show+33% and +34%higher ILSS values compared to MT, respectively. On the other hand, PSA-TSA samples evidence ILSS values just slightly higher (i.e., +12%). A similar behaviour was evidenced by the DCB characterization.

Overall, it was shown that the proposed two-step electrochemical treatment (TSA-PSA) allows to obtain FML shaving the mechanical strength of PSA samples and nearly the corrosion resistance of TSA samples, thus proving its effectiveness as more sustainable alternative procedure to current harmful treatments.

PYROLYZED PMMA ON CARBON FIBER AS ELECTRODE FOR PIEZOELECTRIC ACOUSTIC SENSOR

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Materials to be used as electrodes play a crucial role in improving the performance of lightweight and flexible acoustic sensors, with porosity and high electrical conductivity being determining factors. In this work electrodes made of pyrolyzed PMMA on carbon fibres for acoustic sensing, is studied. Effect of pyrolysis temperature on the conductivity and on device performance are investigated.

PMMA fibres were Electrospun, using PMMA solution in DMA and acetone, in a horizontal set-up, with 15 kV voltage, 15 cm syringe to collector distance and 8 mL/h liquid flow. Rectangular pieces of PMMA fibre layer were placed on pieced of unidirectional carbon fibre sheet and subjected to pyrolysis at temperatures of 800 to 1300 °C under argon flow. The samples were analysed by FTIR ATR, optical microscope, and SEM. Electrical conductivity was measured with a Semiconductor parameter analyser. PVDF membrane was Electrospun similarly to PMMA but with 0.08 mL/h flow. Acoustic sensors were fabricated by layering polyurethane frames with pyrolyzed samples as electrodes and sandwiching the Electrospun PVDF as piezoelectric membrane between two electrodes. The sensor responses were studied using an oscilloscope for collecting data and PRAAT software for analysing the data.

FTIR spectra of all pyrolyzed samples showed a pattern similar to carbon fibre spectrum indicating perfect carbonization of PMMA at all tested temperatures. Optical microscope and SEM images revealed the formation of graphite-like clusters over the carbon fibres distributed in such a way to form a bridge to the aligned carbon fibres. Electrical resistance measurements showed that higher pyrolysis temperature increased the samples conductivity which resulted in a significant improvement also in terms of performance of the acoustic device.

The formation of graphite-like clusters between the aligned carbon fibres considerably improved the electrical conductivity of the material in both parallel and perpendicular directions, an effect that increased further with pyrolysis temperature. It is worth noting that the formed clusters are sufficiently effective in creating electrical interconnections among fibres, which is necessary to reach the described conductivity improvement, but these interconnections distributed and densified in such a way to maintain the desired electrode porosity. Porous electrodes in fact guarantee an efficient detection of vibrating air particles and thus maximize the charges generated by the PVDF membrane, leading to an overall improved sensor response.

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FUNCTIONALIZED CARBON NANOTUBE/PHENYL DOPED g-C_3N_4 SYSTEM FOR EFFICIENT VISIBLE PHOTOCATALYTIC APPLICATIONS

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Photocatalytic materials possess the capability to transform solar energy into chemical energy, finding practical applications in organic pollutant degradation, mitigating CO_2 emissions, and facilitating hydrogen production. Graphitic carbon nitride, acknowledged as a nonmetal semiconductor, is esteemed for its effectiveness as a photocatalyst owing to distinctive features. However, its practical application for contamination removal is hampered by the constrained separation of photogenerated carriers. Carbon nanotubes are widely recognized among nanomaterials for their exceptional properties, playing a crucial role in electron transfer and preventing the recombination of photogenerated electron-hole pairs. In this case, we employed a rapid and straightforward method to prepare a composite photocatalyst by functionalizing Carbon nanotube with polythiophenes and Phenyl-modified graphitic Carbon Nitride. The Catalyst's morphology, structure, and optical properties were characterized, and RhB photodegradation performance was assessed to showcase the composite catalyst's catalytic activity.

The Phenyl-modified graphitic carbon nitride was synthesized using the hydrothermal method. Carbon nanotubes were functionalized through an oxidation process with sonication involving sulfuric acid and nitric acid. Subsequently, 2-hydroxymethyl thiophene was added using the esterification method. The synthesis of the f-CNT/PhCN involved separately dispersing them in methanol, sonicating, and then mixing the solutions under stirring. The mixture was heated in a water bath for 5 h, and the resulting solution was dried to obtain the powder.

Characterization methods: Raman Spectroscopy, Transmission Electron microscope, Time-resolved spectroscopy, Ultraviolet-visible Spectroscopy.

We explored the photocatalytic activity of the hybrid nanostructures by degrading Rhodamine B under visible light. UV absorption analysis results indicated an enhanced activity in the visible region, attributed to the expanded light absorption range facilitated by PhCN. Furthermore, the functionalized Carbon nanotubes enhanced the separation of electron-hole pairs, and the conductive pathways provided by Carbon nanotubes facilitated the rapid migration of electrons. The fast charge transfer observed in time-resolved measurements due to efficient electron movement facilitated by the nanostructure's properties. For the composite morphology analysis, TEM was conducted, revealing the assemblies of materials.

BORON NANOPARTICLES AND ITS OPTOELECTRONIC PROPERTIES

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After Graphene discovery in 2004 the 2D material gained much intention in material science due to their fantastic applications in catalysis, optoelectronics and energy conversion etc. The exploration of silicene and Phosphorene has increased the 2D material family. Now a days lighter elements like carbon, boron and oxygen have gained an attention to create their 2D material due to their diverse properties. Boron differs from carbon due to its high electron deficiency, so it is quite difficult to exfoliate the Boron to get the Borophene 2D material. One other difficulty is in exfoliation of Boron in crystalline form because it is insoluble in most solvents and very brutal material.

Boron nanoparticles were prepared through water assisted liquid phase exfoliation. Initially Crystalline Boron Pieces were first grinded into fine powder using a mortar. This powder was further used for exfoliation. Water assisted liquid phase exfoliation was carried out by dispersing 100mg of grinded crystalline Boron in 5ml of water and using a 25ml glass vial and sealed the vial using paraffin tape. The Dispersion was ultrasonicated for 24h. Boron nanoparticles were collected by filtering through 0.22μm syringe filter. Finally, the Boron nanoparticles were obtained after drying in oven at 60° C overnight. The dried powder was further done with thermal treatment at 200°C, 300°C, 400°C.

The optical properties of boron nanoparticles were studied by Uv-Vis spectra and photoluminescence spectra. The above prepared four samples were studied for different kinds of defects originated during exfoliation and thermal treatment. In Uv, as the thermal temperature increases the shape of absorption band changes. With increase of temperature the absorption increases up to 300°C and then decrease in absorption at 400°C. We also studied the photoluminescence for all the samples to check the originated defects.

The creation of effective optoelectronic applications using boron nanoparticles relies heavily on our ability to manipulate their structural defects. One crucial aspect is the fluorescent emission, which has been found to be influenced by vacancies and substitutional defects within the material. In our recent study, we focused on obtaining boron nanoparticles through a method involving sonication-assisted liquid-phase exfoliation from bulk Boron. Upon preparation, we observed a weak fluorescent emission in Uv range around 330 nm. To enhance the fluorescent properties, we deliberately introduced tailored defects by subjecting boron nanoparticles to oxidation at varying temperatures in ambient air. Interestingly, we found a significant increase and shift in the fluorescent emission of the oxidized boron nanoparticles, with the most pronounced increase observed in samples treated at 200°C. However, beyond this temperature threshold, a reverse effect occurred, leading to a decrease in fluorescence intensity.

OPTIMIZATION OF DIRECT INK DEPOSITION PROCESS OF GLASS-CERAMIC SEALANT FOR A NEW GENERATION OF BATTERIES: A DoE APPROACH

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Robocasting is a popular method for producing ceramic and glass components, especially for sealing materials. In the frame of the SOLSTICE project (European Union's Horizon 2020, grant agreement No 963599), which aims to develop Na-Zn batteries, the optimization of the formulation of a glass-ceramic ink has been performed to adapt the paste's rheology to a pre-existing industrial process of direct deposition.

The glass-ceramic sealant has been dispersed into a water-based ink also composed of four more additives for the rheology modification. After a brief characterization of the sealant's powder granulometry, the effect of each component of the ink has been evaluated through the Design of Experiment and ANOVA. In particular, a Fractional Factorial Design 25-1 has been defined and used indexing different parameter extracts from a 5 Step Thixotropy Test performed on 17 different recipes.

Most of the models defined through the DoE have been experimentally validated. Through each model, much information about the influence of each component of the recipe on some rheological characteristics of the paste has been extracted. The indexes defined in the Methods section covered different rheological parameters such as the viscosity at high and low shear rates, the time dependency of the viscosity of the paste, the stability of the viscosity value of the paste during the printing process through robocasting, and the reproducibility of the properties in two consecutive steps of printing. The information concerning the effect of each component has been then used to tune the ink recipe to obtain a rheological behavior that better reproduces the one ink of reference, to introduce the new formulation in an industrial deposition process without any further modification of the process parameters.

The study delves into the rheological properties of a robocasting ink using the Design of Experiments. Key components affecting viscosity and printability were identified. Results confirmed solid load as the primary factor affecting viscosity. Observations on bentonite revealed a diminishing impact with increased shear rates, shedding light on ink dynamics. A multivariate approach refined the ink recipe, yielding a new composition meeting set criterion, and exhibiting versatility and innovation potential. This exploration, employing DoE, lays the groundwork for enhancing sealant formulations in additive manufacturing, emphasizing understanding and optimization. Overall, it advances comprehension of ink behavior and offers new insights for future innovation in robocasting ink development.

PULSED LASER-ANNEALED VO_2 THIN FILMS FOR H_2 SENSING APPLICATIONS

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The temperature-dependence of the optical/electrical properties of vanadium dioxide (VO_2) thin films can be exploited for several applications, including gas sensing and thermal regulation of buildings. Upon a specific transition temperature (Tc ~ 68°C), which can be opportunely decreased, VO_2 undergoes an insulator-metal transition (MIT) with a concurrent structural and electronic variation. Current challenges of solution-based VO_2 thin films concern the high temperatures required for the crystallization step and the difficulty of controlling the final stoichiometry. The latter problems can be solved by nanosecond pulsed laser annealing (ns-PLA), which allows for local temperature increases within the film without involving the substrate. VO_2 thin films were synthetized from a non-carcinogenic precursor and irradiated with a KrF excimer laser at room temperature in air. The optimal working window was defined by tuning the atmosphere during deposition, drying temperature, film aging, and crystallization time. The parameters were evaluated by GIXRD, SEM, TEM, UV-Vis-NIR and Raman spectroscopy, volt-amperometric measurements, XPS, RBS. Simulations were used to estimate the temperature distribution within the films during laser pulses. Different types of VO_2 films were prepared by varying the laser parameters and their efficiency towards H_2 gas sensing was compared to furnace annealed ones. Platinum nanoparticles were added on the VO_2 films.
Crystallization was found to start from the first few pulses and full conversion to crystalline VO_2 (M1) was reached within a few seconds. Similar NIR modulation efficiencies could be reached through multiple combinations of sol-gel parameters. Both the laser- and furnace-annealed films, coupled with Pt NPs, displayed resistivity and transmittance variations upon H2 exposure. The morphology and crystallinity degree were found to influence the gas sensing activity.
The versatility of sol-gel reactions was combined with ultrafast PLA for the simultaneous crystallization and nanostructuring of VO_2 thin films. The applicability of the latter as H_2 gas sensors was proven. Besides gas sensing, this method widens the possibilities to exploit the MIT of VO_2 in multiple fields, from electrocatalytic water splitting to radiative cooling or microactuators.

TITANIUM DIOXIDE NANOTUBES: A VERSATILE MATERIAL FOR ENERGY STORAGE AND MATERIAL RECOVERY APPLICATIONS

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Titanium dioxide (TiO_2) has been widely investigated in the materials science field due to its many interesting properties which make it a promising candidate for applications in several different fields. Among its many possible nanostructures, self-organizing nanotubes (NTs) grown by electrochemical anodic oxidation are characterized by a high tuneability of both morphology and properties depending on the synthesis parameters. This versatility makes them valuable electrodes for both the energy and environmental fields, and applications as electrodes for photovoltaics, batteries and supercapacitors.

Amorphous titanium dioxide NTs were prepared by a two-step anodic oxidation process in an ethylene-glycol based solution containing NH_4F. The NTs then underwent different treatments depending on their chosen application. Thermal annealing treatments were conducted at different temperatures and atmospheres depending on the crystallinity wanted. Hydrothermal conversions into mixed titanium oxides were performed for applications in lithium ion and potassium ion electrochemical devices. All NTs were then characterized from a morphological and physico-chemical point of view, and electrochemically tested in organic electrolytes.

Black amorphous TiO_2 NTs were obtained through a thermal annealing under a reducing atmosphere (H_2/Ar) at different temperatures under 300°C to maintain their amorphicity. This reduction increased their adsorbance spectra as indicated by the lowering of the conduction band and resulted in a more capacitive-like behavior. The NTs for lithium-ion electrochemical devices were instead annealed at 450°C to obtain anatase nanotubes and further hydrothermally converted into mixed titanium oxides, while the ones for potassium-ion applications were hydrothermally converted from the amorphous state. The lithiated NTs were then electrochemically tested for lithium recovery applications and showed excellent stability and reversibility from both a morphological and chemical point of view through a static de-lithiation process, while the potassiated one were tested for batteries applications.

The black amorphous TiO_2 NTs presented an increased defectivity thus resulting in higher donor densities and specific capacitances, shifting their storage mechanism to a more capacitive controlled one. The feasibility of hydrothermally converting TiO_2 NTs into different mixed oxides was investigated. While in the case of lithium-ion starting from amorphous or anatase NTs presented no significant differences, only amorphous ones were suitable for potassium ions applications. Finally, their properties in electrochemical energy storage devices were evaluated.

PREPARATION OF NANOSTRUCTURED TiO_2 IN THE GREEN UP PROJECT

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GREEN UP aims to develop a new generation of photon upconversion hybrid nanomaterials, utilizing triplet-triplet annihilation for solar photocatalysis and nanostructured TiO_2 as the support/receiver material. Mechanical processing of powders represents a convenient route to the solvent-free preparation of nanostructured TiO_2, provided that transformation kinetics is suitably characterized, and mechanical activation is properly controlled. This is the subject of the present contribution.

We investigate the transformation kinetics of TiO_2 powders that undergo mechanical processing by ball milling under various experimental conditions. To this aim, we use different ball mills and systematically change processing and experimental variables. Phase transformations are studied by X-ray diffraction.

In agreement with literature, we observe the gradual transformation of starting anatase in an intermediate phase, first, and then, in rutile. Grain size reduction of anatase is faster than its transformation. The intermediate and final TiO_2 phases form invariably exhibit nanocrystallinity. We show that the transformation rates correlate with several processing and experimental variables.

This study was carried out within the «GREEN UP: GREENER NANOMATERIALS FOR UPCONVERSION IN PHOTOCATALYTIC APPLICATIONS» project – funded by the Ministero dell'Università e della Ricerca – within the PRIN 2022 program (D.D.104 -02/02/2022) funded by the European Union - Next Generation EU. This manuscript reflects only the authors' views and opinions, and the Ministry cannot be considered responsible for them.

TRANSPARENT WOOD AS A NEW BUILDING MATERIAL WITH PHOTO-SWITCHING PROPERTIES

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Optical transparent materials occupy an irreplaceable market position in various fields, especially in the energy-saving building one. These are important for reducing indoor energy consumption by enabling better thermal insulation, promoting effective sunlight harvesting, offering comfortable indoor lighting, and reducing the construction industry's carbon footprint. A new promising material with these features is transparent wood. TW has excellent optical properties, good UV-blocking ability, and low thermal conductivity, as well as a rapid fabrication process and mechanical robustness, holding great potential in energy-efficient building applications.

The fabrication of transparent wood involves two main steps: The first focuses on removing lignin (delignification) from the wood to obtain bleached wood, while the second involves the introduction of filling materials into the wood channels (lumens) delignification process was done with oxidizing solutions such as H_2O_2 in NaOH and heat. The second step, envisioning the development of light-responsive transparent wood, was done by including selected π-conjugated compounds into the filling composition for the lumens infiltration. The resulting wood composites were investigated and characterized with several techniques including UV/vis and IR spectroscopy, XRD, SEM, TEM, DSC and NMR for the synthetized compounds.

Preliminary results on the treatment of wood of different kinds, highlight the necessity of employing multiple and sequential doses of oxidizing solutions for the delignification process. One potential explanation for this observation can be attributed to the distinct arrangement of lignin in softwoods, which significantly differs from that in hardwoods commonly reported in the literature. This variation is associated with the faster growth rate of the plants that produce it. Lumen filling was accomplished using three distinct methodologies: chromophore adsorption followed by polymer infiltration; covalent anchoring of chromophores to the lumen wall followed by polymer infiltration; and preparation of monomers inclusive of pendant chromophores for one-step infiltration and polymerization.

Light-responsive transparent wood was achieved through delignification of the wood followed by infiltration of π-conjugated compounds and structuring polymers with a refractive index comparable to that of wood (~1.5), ensuring transparency. Two different class of π-conjugated compounds were synthetized and investigated: azobenzene molecular switches and e electron-rich arylamine derivatives. The first were prepared by classic diazonium salt method followed by introduction of carbonyl group, the second were prepared by Heck coupling of methyl acrylate with brominated triphenylamine. These compounds were introduced into the lumen through three aforementioned approaches.

GEOPOLYMER COMPOSITES WITH CARBON FIBERS FOR APPLICATION IN ENERGY STORAGE SYSTEMS

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Sensible Heat Thermal Energy Storage or SHTES is a technology of growing importance in industrial energy saving strategies as it allows the recovery a fraction of energy that can be used when necessary. The most common storage unit is made of a high-performance concrete, which uses Portland cement (OPC) as a binder, a material that has a huge carbon footprint. In the civil engineering there is a line of research aimed at developing alternative binders to cement with a lower environmental impact. Among the alternative binders, geopolymers are the most promising in the industrial field of SHTES as they are characterized by ceramic structure with eventual high resistance to thermal stress and high chemical inertia. Unfortunately, the thermal properties, e.g. thermal conductivity, of geopolymers are not satisfying and improving these properties is essential to be able to propose alternative systems to the reference ones currently in use.

A common aluminosilicate precursor, a metakaolin, was used, capable of guaranteeing adequate mechanical performance and good reproducibility, an alkaline solution of sodium hydroxide and silicate as an activator, since the main objective of this work is to increase the thermal properties through the use of appropriate additives or aggregates.

Samples of geopolymer matrix alone, geopolymer matrix mortars with standard sand and OPC-based mortar with standard sand were therefore prepared and characterized, to be used as a reference to obtain information on the unmodified thermal properties of the geopolymer matrix; these data will be used to the modeling of geopolymer concrete. Finally, several additives will be tested to improve thermal properties and long-term durability, such as graphene, carbon fibers and waste glass powder.

The objective of this study is therefore to develop a geopolymer mortar for use in a SHTES system while limiting its carbon content thanks to the prevalent use of waste materials such as: waste glass from recycling plants, a geopolymer, and fibers of carbon, which should improve both the resistance to thermal stress and the thermal conductivity of geopolymer mortars. The use of fibers in geopolymer systems, based on natural, synthetic or metallic fibres, is widespread in order to improve mechanical performance, especially by creating extended pseudoplastic behaviour. This work examines the use of carbon fibers from recycled composites to evaluate the role of fiber percentage and dispersion method on the thermal and mechanical properties of a geopolymeric mortar for SHTES.

This study was developed in the framework of the research activities carried out within the Project "Network 4 Energy Sustainable Transition - NEST", Spoke 8, Project code PE0000021, funded under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell'Universita` e della Ricerca (MUR); funded by the European Union – NextGenerationEU.

STUDY AND SYNTHESIS OF NEW COUMARINS WITH THERMALLY ACTIVATED DELAYED FLUORESCENCE (TADF) PROPERTIES FOR SENSING APPLICATIONS

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Coumarins are known for their biological activities and beyond; our focus has been on exploring their electronic and physicochemical properties, particularly in fluorescence. Introducing electron-donating groups onto the benzene ring of coumarin yields highly efficient dyes used as metal-free luminescent sensors, biological agents, and bioimaging tools. Recently, new coumarin derivatives with high photoluminescence quantum yield (PLQY) and thermally activated delayed fluorescence (TADF) properties have emerged. Our research centers on these TADF-carbazole-coumarin compounds, investigating their synthesis, photophysical characteristics, and utility as reversible molecular oxygen sensors. By incorporating these luminophores into commercial polymers and employing stereolithographic 3D printing, we've developed thin, manageable sensors, showcasing their versatility for practical applications.

Density Functional Theory (DFT) calculations explored electronic properties of 3-carboxyethyl coumarin derivatives with carbazole units. Promising compounds were synthesized via Knoevenagel condensation followed by Buchwald-Hartwig coupling under mild conditions. Absorption and emission spectra were measured, alongside solvatochromic studies and transient absorption spectroscopy. PMMA(Polimetilmetacrilato) films containing synthesized compounds were evaluated as oxygen sensors using Stern-Volmer analysis.

Computational simulations indicate that compounds with a carbazole unit at positions 6(Cmr-6Cz) and 7(Cmr-7Cz) of the chromenone benzene ring exhibit the most promising properties for TADF. The experimental synthesis of these compounds proves to be complex, yielding variable results. Photophysical characterization confirms the TADF behavior in the derivatives Cmr-6Cz and Cmr-7Cz, revealing their potential as oxygen sensors in solid matrices. Solid-state oxygen sensing studies highlight the applicability of these compounds as economical and reproducible sensors.

This work demonstrates the synthesis of new organic dyes by incorporating carbazole heterocyclic derivatives onto coumarin scaffolds, yielding compounds with good luminescence quantum yields and TADF properties. DFT calculations guided the prediction and design of these compounds, highlighting the potential value of Cmr-Cz adducts as TADF emitters, a finding confirmed by experimental results. The TADF properties of carbazolyl-coumarins were explored both in solution and in PMMA solid-state matrices. Additionally, a sensor for O_2 detection based on Cmr-PMMA was developed, showcasing the versatility of these compounds.

DECODING MOLECULAR ASPECTS OF THE GROWTH AND SURFACE FEATURES OF HIGHLY LUMINESCENT $CsPbBr_3$ NANOPARTICLES FOR THEIR TECHNOLOGICAL APPLICATIONS

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Lead halide perovskite nanoparticles (NPs), have garnered significant interest due to their exceptional optoelectronic properties. The attractive properties of lead halide perovskite NPs particularly $CsPbBr_3$, have driven increasing progress in the development of synthetic procedures to obtain high-quality NPs at high concentration. Owing to its excellent optoelectronic properties. $CsPbBr_3$, more stable than its iodide counterpart, possesses unique potential for developing optoelectronic devices. Its photophysical properties can be improved by selecting colloidal syntheses conditions and surface engineering. Enhanced thermal and photo-stability, partly associated with ligand loss, can be achieved through the judicious selection of surface chemistry.

In this study, $CsPbBr_3$ NPs were synthesized using both hot-injection (HI) and ligand-assisted reprecipitation (LARP) methods in non-polar solvents with tailored precursor and surfactant mixtures. The morphology, emission properties, reactive species, and surface ligand composition were thoroughly analyzed to understand the synthetic process and its impact on NP characteristics.

The careful analysis of NPs morphology, emission properties, reactive species in the mixtures and composition of the ligands bound at NP surface allows to tackle still open issues, including achievement of NP monodispersity, high NP production yield and to unveil the mechanisms behind changes of the emission properties in time. The presence of bulk crystals, forming as precipitates during LARP hinders the attainment of a highly concentrated solution of nanoparticles. The size of the NPs obtained by LARP is poorly affected by the ligands nature and bromide-rich synthetic condition effectively results in NPs with excellent emission properties. In contrast, NPs synthesized by HI exhibit high reaction yield, size control through diffusion-driven growth, and comparatively subdued emission properties.

This study sheds light on the synthesis of $CsPbBr_3$ NPs via HI and LARP approaches, elucidating their advantages and limitations. Understanding these aspects is crucial for optimizing synthetic methodologies to achieve high-quality NPs with desirable properties for various technological applications.

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MULTIFUNCTIONAL SANDWICH COMPOSITES CONTAINING PHASE CHANGE MATERIALS FOR SIMULTANEOUS STRUCTURAL AND THERMAL PERFORMANCE

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Phase change materials (PCMs) can store and release significant amounts of heat, providing effective thermal energy storage (TES) in applications that require managing temporary spikes or dips in temperature, such as electric vehicles and buildings. Rather than using separate structural and thermal management components, multifunctional composites aim to integrate both mechanical and TES capabilities within a single material system. A promising route is the development of sandwich composite panels with foam cores containing PCMs, in which the outer skins provide the necessary mechanical stiffness and strength, while the PCM-containing core increases thermal buffering and enables heat management.

This work aims at fabricating and testing rigid polyurethane (PU) foam cores with varying contents of a microencapsulated PCM (up to 30 wt%) and subsequently developing sandwich composites by adding outer epoxy/carbon skins. Extensive morphological, thermal, and mechanical testing was carried out to determine the PCM content delivering the best balance between energy storage capacity, mechanical performance, and thermal insulation capability.

It was found that PCM loadings up to 20% by weight preserved suitable thermal conductivity values for thermal insulation applications, while not excessively compromising the structural integrity of the foam. On the other hand, at 30 wt% PCM content both the thermal conductivity and compressive mechanical properties of the foam are impaired considerably. Hence, the PU core with 20 wt% PCM was selected to produce sandwich panels. Mechanical testing of the manufactured sandwich panels showed that the 20 wt% PCM foam core material maintained adequate strength and stiffness. The failure mode in three-point bending shifted from compression failure of the upper skin to shear failure of the foam core as the PCM was introduced. Flatwise tensile strength was reduced from 362 kPa for the neat PU foam core sandwich composites down to 207 kPa for the panels with a 20 wt% PCM foam core. Such strength reduction was likely caused by the more irregular porous morphology of the PCM-containing foam reducing effective skin/core contact area. Finally, edgewise compressive strength showed a similar decreasing trend from 43 MPa to 30 MPa.

Overall, the 20 wt% PCM-loaded polyurethane foam possessed the optimal combination of thermal insulation, mechanical integrity, and heat management capacity. Further work is warranted to optimize the foam microstructure and adhesion at the skin/core interface to fully exploit the thermal storage potential of the PCM while preserving structural performance.

SYNTHETIC, INNOVATIVE MATERIALS FOR GAS SEPARATION MEMBRANES AND THEIR TRANSPORT PROPERTIES

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Membrane separation technology is replacing traditional gas separation processes, and increasingly challenging separations require a constant search for new and better-performing materials. In this context, the synthesis of innovative materials for the preparation of novel membranes with enhanced gas transport properties is essential to promote the exploitation of membrane gas separation technology in emerging fields such as CO_2 capture or H_2 purification. Herein we will present our latest results in the field, with particular focus on mixed matrix membranes, i.e., membranes composed of a polymer matrix and a filler with tailored characteristics.

Mixed matrix membranes are prepared from a huge variety of polymers and fillers. The talk will focus on two classes of polymers, the Polymers of Intrinsic Microporosity, that thanks to their high permeability have been used to redefine the state-of-the-art, and bio-based polymers, which have lower performance but also a lower carbon footprint. Several fillers will be taken as example and their selection will span from Metal Organic Frameworks, insoluble polymers, and Cages to cellulose nanocrystals and Ionic Liquids.

In this work, we will present the transport properties of membranes prepared from different materials, both as neat polymers and in the form of mixed matrix membranes. On one hand, the pure gas permeability measurements will help in the understanding of the effect of the fillers in the polymer matrix and on the permeability, diffusivity, and solubility of the gases in the membranes. On the other hand, the mixed gas analysis is carried out to validate the potential of the most promising membranes for the treatment of relevant gas separation studies. For instance, while fillers with high porosity can be used to boost the CO_2/N_2 or CO_2/CH_4 separation, ionic liquids can reverse the selectivity and making a polymer CO_2 or H_2 selective for the treatment of syngas.

Innovative materials have the potential to boost gas separation membrane technology in many industrial processes related to energy and ecological transition, as well as to circular economy. The discussion in this work, with the focus on membranes for CO_2 capture and some excursus on H_2 purification, will be an overview of the plethora of materials that can be used in membrane preparation with their advantages and disadvantages related to the gas separation and purification performance. Data from molecular modelling will be also used to give a deeper insight in the structure/properties relationship.

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METAL NITRIDES AND OXYNITRIDES AS CATALYSTS AND CATALYSTS SUPPORT FOR GREEN ENERGY CONVERSION

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The durability and the life expectancy of catalysts passes through the stability of their constituting materials. Since the use of easy storable, and conveyable chemicals as green energy vectors is one of the more promising future scenarios; the requests for durable, heat resistant and highly performing catalysts and catalysts' support is of high interest. For their anticorrosive properties, metallic nitrides and oxynitrides can be used as efficient substitutes for gold and platinum group elements (PGE), limiting the role of the latter to the actual catalytic mechanism. In addition, some of these compounds are considered active participants in hydrogen evolution by water electrolysis, sometimes favoring the hydrogen evolution reaction (HER), sometimes the oxygen evolution reaction (OER).

Metal nitride and oxynitride coatings are realized by reactive magnetron sputtering of metallic cathodes in a nitrogen enriched atmosphere, in vacuum (10-3 mbar). The obtained materials are characterized regarding the catalytic activity and the corrosion resistance using electrochemical techniques. Composition is evaluated using X-ray photoelectron spectroscopy and powder X-ray diffraction, while the surface morphology is evaluated using different microscopies.

The influence of the sputtering condition in the resulting coating is highlighted in terms of composition, electrical and electrochemical behaviour, and morphology. These characteristics are related to the catalytic and anti-corrosive properties showed.

Different sputtering conditions produce materials with different structural and compositional characteristics and technological properties. The low expensiveness of the chosen technique, its safety, the low environmental impact, and its controllability in thin film deposition is highlighted and commented, considering the quality of the resulting materials and the easiness in the process scale up.

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SUSTAINABLE SOLAR CELLS BASED ON NON-TOXIC METAL HALIDE PEROVSKITES

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The need for self-powered electronics is progressively growing in parallel with the flourishing of the Internet of Things (IoT). Although batteries are dominating as powering devices, other small systems, such as piezoelectric, thermoelectric, and photovoltaic systems, are attracting attention. These last ones can be adapted from their classical outdoor configuration to work preferentially under indoor illumination, i.e., by harvesting the spectrum emitted by LEDs and/or fluorescent lamps. However, crystalline silicon, the classical photovoltaic material for solar panels, has a bandgap not suitable for ensuring good efficiency with such spectra. With wider bandgaps, other semiconductors can come into play for this task. Still, the materials of choice, having to be integrated within households, should also satisfy the criterion of non-toxicity and maintain low-cost production. While lead-based halide perovskites cannot represent a valuable solution for this scope, due to the strong environmental and health concerns associated with the presence of Pb, analogous compounds based on the heaviest pnictogens, i.e., bismuth and antimony, could work as sustainable light-harvesters for indoor photovoltaic devices.

In this contribution, I will report on recent results from my group on the fabrication of solar cells based on the silver-bismuth double perovskite featuring the use of carbon electrodes prepared from waste-recovery as the hole selective contacts.

BLACK MASS FROM SPENT LITHIUM-ION BATTERIES AS A POTENTIAL ELECTRODE MATERIAL FOR CAPACITIVE DEIONIZATION OF WATER

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Black Mass (BM) is the industry term used to indicate the powdered material recovered after mechanical treatment of the spent Li-ion battery (LIB). It consists of a mixture of anodic and cathodic materials. Therefore, BM could represent a valid resource for many applications that use graphite and valuable metals, such as lithium, manganese, cobalt, nickel and copper. Among them, capacitive deionization (CDI) is emerging as promising and sustainable water desalination technology for its simplicity and eco-friendliness. At the best of the authors' knowledge, the reuse of spent LIBs for the preparation of electrodes for water desalination via the capacitive method has never been reported in the literature.

The present contribution deals with the preparation of electrodes for water CDI by the use of BM from spent LIBs and the preliminary evaluation of their capacitive behavior. Two different grades of BM, obtained after two stages of crushing, sieving, and magnetic separation, are used for this purpose. The electrochemical performance of the two grades (BM1 and BM2) as active materials for CDI electrodes is evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

The two grades, consisting of the undersize (< 4.0 mm) fractions from the sieving unit are mainly composed by graphite; cathode active materials ($LiMO_x$, with M = Mn/Co/Ni) are also present to a different extent.

CV results show that, in the range of scan-rates investigated (5-100 mV s-1), BM2 electrode exhibits the best performance. At 5 mVs-1 scan, its specific capacitance is 86.5 F/g, against 73.2 F/g of BM1. Its conductivity, as resulting from EIS measurements, is also higher than that of BM1. The better electrochemical performance of BM2 electrode is ascribed to the synergistic action of graphite and metal oxides. The preliminary results obtained demonstrate the great potential of BM as a low-cost and environmentally friendly electrode material for water desalination via capacitive deionization.

METAL/METAL OXIDE DECORATED GRAPHENE FOR WATER ELECTROLYSIS

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The succesful utilization of hydrogen as an energy vector in harnessing power surplus derived from renewable sources is progressively pivotal within the worldwide transition toward sustainable energy frameworks. To enhance the competitiveness of hydrogen against other energy mediums, predominantly reliant on electrochemical processes, there is a pressing need for the innovation of more efficient methodologies for its convenient production.

Carbon's extensive historical association with hydrogen mostly extends to its utilization as a substrate catalyst for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Notably, graphene emerges as a promising material for fabricating high-performance electrolyzers owing to its exceptional mechanical, chemical, and transport properties, as well as its substantial specific surface area. Graphene can be readily decorated with metal and metal oxide nanoparticles, forming the core of a water electrolyzer. To enable broad adoption, it is imperative to devise scalable and cost-effective methods for the production of graphene and its decoration with catalytic materials. Thermally Exfoliated Graphite Oxide (TEGO) has been developed in our laboratory (Nanocarbon Laboratory) and consists in a chemical route to obtain gram-scale graphene material, with an average 3-layer structure. The thermal exfoliation occurs at 1150°C, resulting in a high surface area carbon (<800 m^2/g) rich in defects (mainly vacancies and edges). These features make this material ideal for the decoration with nanoparticles of various nature.

In this work, an effective synthetic route to produce platinum decorated TEGO in a scalable way will be probed, to develop efficient water-splitting electrodes. Pt-decorated TEGO has been obtained by the decomposition of platinum-carbonyl clusters, which have been proven effective in decorating the carbon scaffold. Depending on the chosen starting cluster $(\text{Ligand}^+)_n[\text{Pt}_x(\text{CO})_y]_{n-}$, both platinum nanoclusters, sub-nano cluster or even single-atom decoration was obtained thanks to the defective-rich substrate, which helps overcoming the large cohesion energies of the transition metal.

Also, TiO_2-decorated TEGO was obtained, via a green chemical process, consisting in the hydrolysis of titanium (IV) isopropoxide carried out in a autoclave reactor under mild conditions using water as solvent and reagent. Also in this case, the defective graphene scaffold allowed to obtain docked nanoparticles averaging 7 nm in size with a decoration synthesis that can be easily tuned and optimized in particle quantity and dimension.

HER and OER catalytic activity of metal/metal oxide decorated TEGO will then be tested in a three-electrode cell, and the overpotentials will be evaluated by Tafel plot analysis.

DEVELOPMENT OF FLAME RETARDANT POLYELECTROLYTE COMPLEX COMPOSITE WITH COLLAGEN-RICH SHAVINGS FROM TANNERY WASTES

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Owing the environmental pollution due to petroleum-based insulation materials, the need for new renewable materials has become more urgent. In this context tannery wastes, in particular collagen-rich shavings, are a good candidate for the development of bio-based materials. Leather shavings are currently employed to recover chemicals (like chromium or protein hydrolysate), to make energy or fuel by a thermal treatment or directly use to make adsorbents or composite materials. In this work tannery shavings were used as filler into a polyelectrolytes complex matrix in order to make a fire-safe and sustainable composite material.

Gelatin and cellulose nanofibers were mixed together and processed under controlled conditions in order to prepare stable polyelectrolyte complexes (PECs). Tannery shavings were dispersed, at different concentrations, into the gel and then freeze-dried to obtain a lightweight porous material (density of 120 kg/m3). Morphology and composition were evaluated by SEM investigations. Mechanical and flame retardant properties were measured by compression and flammability tests, respectively.

SEM observation pointed out the formation of a 3D structure where the fibers are held together by the gelatin/nanocellulose polyelectrolyte complex. Mechanical tests highlighted a compression modulus of 0.7 ± 0.1 MPa. The prepared samples were then subjected to horizontal and vertical flammability test. For both configurations the material achieved a self-extinguishing behavior.

SEM images showed an irregular shape of the collagen-based fibers. This is probably due to the source of the fibers which, being a waste from tannery process, produces a heterogenous distribution of fiber dimensions. Compression test results suggest good mechanical properties of the prepared fiber networks that are likely ascribed to the electrostatic interactions occurring at molecular scale within gelatin and nanocellulose as well as the optimal affinity between the PECs and the fibers. During flammability test, in both configurations, no flame spread occurs and almost the totality of sample remains intact with residues higher than 90%. This is ascribed to the intrinsic flame retardant characteristics of the collagen fibers. Further development might be focused on changing the composition of polyelectrolyte matrix in order to target specific flame retardancy or improved mechanical properties.

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DEVELOPMENT OF NEW BIO-COMPOSITE MATERIALS FOR POTENTIAL HOSPITAL WASTEWATER TREATMENT

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Pharmaceutical active compounds (PhACs) are substances widely used in medicine for diseases prevention or treatment. Since conventional treatment plants are not able to remove completely PhACs from wastewater, these substances are often found in the environment, e.g., surface and groundwater bodies. Problems like biomagnification, or formation of antibiotic-resistant bacteria already are a concern, therefore it is important to find viable ways to remove efficiently PhACs from wastewater. The aim of this work is to develop new bio-composite materials suitable to remove PhACs.

Bio-composite materials were produced using sodium alginate biopolymer (SA) and graphene oxide (GO). Different SA:GO weight ratios were tested to enhance absorption capacity, resistance in water, and mechanical resistance. Freeze-drying process was used to obtain a bio-composite material with high porosity. Absorption tests were performed considering two model-pollutants, namely Tetracycline HCl and Triamterene. Samples' removal efficiency was measured using UV-Vis spectroscopy. Finally, the Design of Experiments (DoE) methodology was used to optimize the capacity of SA:GO composites to absorb Triamterene, considering production process parameters as input variables.

Screening tests were conducted, and bio-composite materials were first synthesized and the SA:GO ratio was minimized until the point where the material could maintain its own shape without losing GO particles. Absorption tests with Tetracycline HCl-water solutions and Triamterene-water solutions showed a removal efficiency respectively near to 70% and 80%. Design of Experiments (DoE) was used to move insight the crosslinking step in the production of samples: final samples had a removal efficiency near to 90%, and the loss of volume due to compression of samples was reduced to 20%. Finally, all the tested compositions showed no loss of GO after 24 hours in water.

SA:GO composite materials show good results in the absorption both of Tetracycline HCl and Triamterene. However, Triamterene seems to be more promising, and the use of DoE allowed to maximise the absorption performance while keeping good mechanical properties of the materials.

DEVELOPMENT OF NOVEL WOOD POLYMERIC HYBRIDS (WPHS): ASSESSMENT STUDY OF MEDITERRANEAN WOODS

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Cellulose-based composites are of great interest as eco-friendly, renewable resource origin, low density and low-cost materials. Wood is widely used as structural material, due its unique hierarchical architecture providing an excellent mechanical performance. Wood species show different physical properties and are well addressed to bio-economy. The idea is to develop an original systematic study on wood-polymer hybrids (WPHs) derived from chemically delignified Mediterranean wood species infiltrated with refractive index-matching polymers for application in various emerging engineering fields.
Delignification process was pursued on wood samples of different cut (transversal and longitudinal) and thickness (from 0.6 mm to 3 mm) by using either a sulphite-based liquor or a chlorite-based liquor. Chemically delignified woods (DWs) and WPHs have been characterized by scanning electron microscopy (SEM) and optical microscopy (OM), IR spectroscopy (FTIR-ATR), Raman spectroscopy, X-ray diffraction analysis, thermogravimetry, and optical transmittance. Mechanical properties were assessed by tensile test.
The chemical treatments led cellulose-rich wood templates that preserved the typical morphology and microstructure of each provenance wood. The impact of the two delignification routes on wood samples have been clearly evidenced in terms of total transmittance, thermal stability, Segal Crystallinity Index and tensile strength. The resulting overall properties of DWs depended on wood type, sample thickness and process parameters. Preliminary results on WPHs obtained by infiltration of epoxy resin in selected DWs showed interesting response in terms of total transmittance and mechanical properties.

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DIGITAL LIGHT PROCESSING (DLP) 3D PRINTING OF SELF-MONITORING CARBON NANOTUBES LOADED BIOBASED RESIN

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A self-monitoring material can detect its own deformation status without using any external sensor thanks to piezoresistivity. This effect is detectable in polymer-matrix composite materials filled with an electrically conductive filler (i.e. single walled carbon nanotubes SWCNT). When a composite system with a conductive particles percolating network is deformed, a variation of the overall electrical resistance is measured. Industries with high-performance demands, i.e. aerospace, bio-medical, and automotive sectors, are ideal candidates for the implementation of self-monitoring materials. This is particularly relevant when utilizing additive manufacturing techniques, which enable the production of complex designed components. Concurrently, in recent years there has been a growing emphasis on sustainability, with a focus on developing new materials sourced from natural origins. In this context, biopolymers derived from vegetable oils, such as soybean oil, emerge as a promising alternative to synthetic polymers. These biopolymers could be employed to create self-monitoring 3D printable components, aligning with the goal of sustainable manufacturing.

Acrylated epoxidized soybean oil (AESO), polyethylene diacrylate (PEGDA) and pentaerythritol tetra-acrylate (PETA), in the weight ratio AESO : PEGDA : PETA of 50:40:10 were mixed using a planetary mixer, then 0.25% by weight of SWCNTs and the photoinitiator (BAPO) have been added. Resins have been 3D printed via DLP using a commercial 3D printer Elegoo Mars 3. 3D printed samples sample were characterized by FT-IR, TGA, DMTA while the self-monitoring performance has been assessed performing tensile test with the acquisition of the electrical resistance variation. Accelerated degradation tests have been conducted in NaOH solutions.

The 3D printed samples exhibit dimensional and geometrical precision, along with noteworthy mechanical properties, elastic modulus of 25 MPa, a tensile strength of 2.6 MPa, and a Shore D hardness within the range of 50-60. Furthermore, they demonstrate very good self-monitoring properties, with a gauge factor (GF) of 3. Degradation tests showed that the 3D printed samples undergo hydrolytic degradation, confirming their biodegradability.

Although the presence of carbonaceous filler hinders the photo-curing process, increasing the exposure time, acceptable crosslink degree was reached, and the 3D printed samples presents mechanical properties comparable to the neat resin and to other biobased photo-cured resins. Samples present also self-monitoring properties with electrical resistance varying linearly with the applied load and with a sensitivity higher than traditional strain gauge, demonstrating the feasibility of 3D printing bio-based and biodegradable materials with multifunctional behavior.

TOWARDS SUSTAINABLE LEAD-FREE BCZT: A COMPARISON BETWEEN SOL-GEL METHOD AND MICROWAVE SOLID-STATE SYNTHESIS

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Piezoelectrics are pivotal components for many key technologies, such as actuators, ultrasonic motors, sensors, smart structures, etc. Among the most studied piezoelectrics materials, the BCZT is on the spot since it is based on non-hazardous elements and showcases high d_{33} values. Piezoelectric properties of BCZT are due to the presence of coexisting phases at the so-called "morphotropic phase boundary" (MPB) and the optimal composition is found to be BZT-50 BCT, namely $(Ba_{0.85}Ca_{0.15})(Zr_{0.10}Ti_{0.90})O_3$. However, the BCZT processing shows several drawbacks, i.e. high sintering temperature (up to 1500-1550°C) and low Curie Temperature (Tc ~ 100°C), which limits its application fields. The synthetic route has a great influence on the final microstructure that leads to the variation of the electromechanical properties. For instance, if the stoichiometry control and a homogeneous microstructure are required, the sol-gel synthesis is the best choice. While, if a cost-efficient and solvent-free procedure is preferred, solid-state microwave reaction (SSMWR) represents a viable option. The purpose of this work is to compare these two synthetic routes for BCZT, highlighting the possible differences in the final properties.

For the sol-gel method, two different chelating agents have been employed, i.e. citric acid and ethylenediaminetetraacetic acid (EDTA), respectively. Conversely, both share the same reagents: barium carbonate, calcium acetate, titanium tetraisopropoxide and zirconium butoxide and employ glycerol as an esterifying agent, which affects the homogeneity of the microstructure and the increase in grain size of the densified materials. Concerning the SSMWR, a stoichiometric mixture of $BaCO_3$, $CaCO_3$, TiO_2 and ZrO_2 was employed. The powder mix was hydraulically pressed, and the resulting pellet was heat-treated by microwave radiation for 7 minutes.

The sol-gel synthesis showed that the use of EDTA better controls the formation of $BaTiO_3$. The gels obtained from the two syntheses were then calcined at 900 °C and the resulting powder was analyzed by X-ray diffraction, which revealed the formation of a pure tetragonal BCZT phase only using EDTA. The SSMWR allows to obtain the tetragonal BCZT phase in just 7 minutes, although with some impurities.

The combination of EDTA-glycerol results very promising for the synthesis of BCZT, nevertheless, the sample density should be further enhanced.

The SSMWR appears cleaner and extremely fast; however, being only in its early stage of development, it provides lower yields, which can be further improved by fine-tuning of the heating conditions.

BIOBASED POLYURETHANE FOAMS PRODUCED BY USING POLYOLS FROM USED COOKING OIL

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At present, petroleum remains the primary source of polyols and isocyanates, the main raw materials utilized in the polyurethane (PU) production. However, due to the uncertainty regarding future petroleum prices and the imperative to shift towards greener resources, great attention has been dedicated to replacing traditional fossil-based polyols with alternatives sourced from renewables. In this study, Used Cooking Oil (UCO) was employed to synthesize the polyol segment for producing bio-based polyurethane foams (PUFs).

Polyols (POs) were produced by epoxidizing the UCO through heterogeneously catalyzed oxidation, followed by opening the oxirane rings with diethylene glycol (DEG). Various amounts of reagents (acetic acid and H2O2) were used in the epoxidation process to yield epoxidized oils (EOs) with different degrees of epoxidation (ranging from 50% to 90%) and, consequently, POs with different hydroxyl numbers (ranging from 150 to 300 mgKOH/g).

Bio-based PUFs were synthesized by blending the synthesized POs with a partially bio-based aliphatic isocyanate with additives like water, surfactants, and catalysts. Various ratios of isocyanate content to hydroxyl number, percentages of water, and catalyst were employed to evaluate their impact on the density, mechanical properties, and thermal conductivity of the resulting foams. Additionally, the morphology of the PUFs was examined using scanning electron microscopy (SEM), while thermogravimetric analysis (TGA) was conducted to determine their thermal stability.

PUFs with different properties were obtained by changing the type and/or the quantity of the additives. All the foams produced showed the typical cellular structure, with different cell sizes and distributions. From TGA results, these materials were stable up to 200 °C. Based on the preliminary results obtained, thermal insulation is identified as their potential application.

SUSTAINABLE COATINGS: LIGNIN AND NOVEL BIO-BASED CROSS-LINKING AGENTS

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In response to growing concerns regarding and climate change, there is a rising demand for novel materials derived from biomass. Coatings, which play a vital role in various industries, are currently one of the main areas of ongoing research. Through biorefining, the valorisation of lignocellulosic feedstocks is enabled, producing diverse platform chemicals, biopolymers, and other chemical compounds. One of the promising approaches is to utilize industrial waste and side streams, for instance lignin, the most abundant aromatic biopolymer on Earth. Sourced as a by-product from the papermaking industry through the Kraft process, lignin often undergoes incineration for energy production due to its intrinsic recalcitrance, complex structure and limited solubility, hindering its conversion into high-value products. The preparation of lignin nanoparticles (LNPs) has gathered attention due to their elevated surface area and smaller size, potentially enhancing the valorisation of lignin in materials. Ongoing efforts aim to functionalize LNPs, thereby improving their stability and compatibility with other materials. The objective of the present project was to produce fully biobased functional coatings by using lignin and a cross-linker. We study mechanisms and interactions occurring during the curing and characterize the final properties of the material. A novel bio-based cross-linker (epoIA) was synthesized with a base-catalysed reaction between itaconic acid and epichlorohydrin. Two different reactive groups present in epoIA allows for the formation of a hybrid cross-linking networks. Epoxy-rings are attacked by carboxylic/phenolic groups of lignin forming a first network. The presence of a reactive double bond on the epoIA enables further reactivity of the composite. In this work two different strategies were explored, polymer grafting reactions and thiol-ene. In the first case, we first prepared LNPs using the solvent-shifting method, involving the dissolution of lignin in aqueous acetone followed by a rapid dilution with water to induce nanoparticle formation. We further synthesized a shell of polymethylmethacrylate on LNPs by using radical emulsion polymerization techniques. The coatings were finally prepared through melt casting of the nanocomposites, cured and characterized to determine their final properties. In the second approach, a tetra-thiol compound (S4P) was reacted with epoIA to introduce dynamic cross-linking capabilities capable of undergoing reversible bonds exchange, which could lead to self-healing properties. The crude softwood Kraft lignin was used to modulate functionality of the thermosetting material.

FROM ANCHOVY BONES TO 3D-PRINTED BIOCOMPOSIT FISH CRATES, THE TRANSFORMATION OF A FOOD WASTE INTO A SUSTAINABLE RESOURCE

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The amount of fish wastes produced and grossly discarded in markets has undergone a dramatic increase over the last years causing environmental and hygiene issue. The use of these scraps for the production of materials with higher added value would reduce waste production and solving related environmental and hygiene issue. Combining biopolymers with animal waste could be an effective strategy in the view of producing food packaging decreasing the amount of bioplastic needed creating more sustainable products.
Anchovy fishbone (EE), collected at Ballarò market (Palermo, Italy), were ground into powder and melt mixed to biopolymeric matrices (Mater-Bi® or PLA). The obtained formulations were extruded in order to produce 3D-printable filaments.
Microbiological analyzes revealed that anchovy fishbone powder does not contain microorganisms which, by type or quantity, may represent a risk to human health and, therefore, the filler is safe to handle. MB/EE10 and PLA/EE10 composite filament were able to be 3D printed for FDM into flat or geometrically complex products. The printing process proceeded smoothly, and no clogging of the nozzle was observed.
All prepared composites formulation displayed viscosity values potentially compatible for be processed by 3D printing. Good interfacial adhesion between anchovy fishbone particles and the polymeric matrices was obtained. In tensile performance the addition of 10% of fishbone waste allow to improve elongation (in both matrices) due to the anchovy oil that act as plasticizer. As regards flexural and impact performance, the filler proved to reinforce the composites leading to an increase of flexural modulus, flexural strength and impact strength.
Utilizing 10% of anchovy fishbone waste to produce composite filaments for 3D printing is a feasible and value-added prospect of dispose such scraps that usually accumulate in fish markets, generating bad odors and attracting insects, with a high risk of bacterial proliferation. The produced composite filaments, in fact, can be employed for the manufacture for 3D printing (FDM) fields that need biodegradable, renewable and cost-effective raw material.

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SMART PCBs: AN ECO-FRIENDLY PLATFORM TO PCBS VALORIZATION

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Waste Electrical and Electronical Equipment (WEEE) is subject to special attention from both European and non-European directives due to the global increasing quantity of waste generated annually, and the resulting challenges in its treatment, impacting environment and human health. Today, the treatment of electronic waste leads to the production of dangerously polluting solutions and the failure to recover a large portion of the "non-precious" components contained within them. In this context, the designated objective must be to recycle electronic waste in its entirety, avoiding the production of impactful solutions and further waste. This goal is pursued by the SMaRT PCBs project, which involves the development of a low-impact environmental method for recovering all secondary raw materials contained in WEEE, with particular attention to Printed Circuit Boards (PCBs), rich in economically valuable and critical metals, as well as plastic-glass materials. SMaRT PCBs is a project started in June 2022, with a duration of 36 months, made possible by the contribution of the Ministry of Ecological Transition (MITE), and with the multidisciplinary participation of researchers from the University of Cagliari and Brescia, as well as partners from the business world such as Gold Fixing Srl, Vesti Solidale Soc. Coop., and Le2C (Lombardy Energy Cleantech Cluster).

Leaching experiments are conducted on shredded PCBs (divided by type and granulometry) with selective low impact and recyclable agents. Operative conditions, such as temperature, pH solution and liquid-to-solid ratio, are arranged to achieve high metal selectivity with the lowest carbon footprint. Metals are then recovered from leachates through precipitation/deposition. Solutions and solid fractions are fully characterized (ICP-OES, XRD, FT-IR and elemental analyses)

In the framework of "SMaRT PCBs" project, DICAAR research unit focuses on the optimization, scale-up and technology transfer of a three phases process, previously designed, for base metals, Cu, Ag, Au, Pd high efficiency recovery from waste PCBs. This process proved to be selective and efficient both towards single electronic components and comminuted PCBs achieving high yield recovery targets towards zero waste. The quality of recovered fractions is under sustainability assessment.

3D PRINTING OF BIODEGRADABLE SOYBEAN OIL-BASED COMPOSITES

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Bio-based polymers coming from renewable sources are emerging to replace the traditional plastics derived from fossil sources, because they offer easy processing, fulfill technological and durability requirements, guaranteeing improved properties such as biodegradability, lower costs and environmental impact. At the same time, additive manufacturing technologies have been emerging as greener alternatives to production technologies for polymeric materials. In fact, 3D printing can be considered a rapid prototyping tool due to its high printing accuracy, low raw material uses and wastes, and the ability to realize printed objects with complex geometry and good dimensional stability for many application fields, such as automotive, packaging and biomedical. Among the different 3D printing techniques, VAT-polymerization (VP), allows to realize objects with high complexity and to achieve the highest printing resolution. However, the use of this technique is limited by the limited number of sustainable photopolymerizable resins, commercially available. For this reason, novel bio-based and biodegradable composites containing biofillers from agro-wastes have been prepared and realized by 3D printing technology, using an LCD printer.

Acrylated epoxidized soybean oil (AESO) resin was used as biodegradable starting polymer matrix. Bio-based isorbornyl methacrylate (IBOMA) was used as reactive diluent, and phenyl bis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) as radical photoinitiator. Two types of biofillers were also employed to prepare the final biodegradable composites, named GTF and WPL-CF, coming from corn and wine by-products, respectively.

Biodegradable soybean oil-based composites were produced firstly by combining AESO with IBOMA in the weight ratio of 60:40 wt.% and then by adding 5 wt.% of each biofiller within the photocurable formulations. The bio-based resins were photocross-linked by using an LCD 3D printing machine. Different 3D printed parts were successfully realized with good dimensional accuracy and increasing level of complexity in terms of shapes and structures.

The biodegradable composites, obtained using LCD by dispersing the two different kinds of biofillers within the soybean oil-based matrix, were then widely characterized by thermal, morphological, and mechanical point of view. The specimens realized show improved final properties in terms of elastic modulus, tensile strength, and glass transition temperature values due to the reinforcing effect induced to the presence of the two biofillers, which on the contrary does not affects the thermal stability.

UNLOCKING ECO-FRIENDLY SOLUTIONS: INNOVATIVE COMPOSITE GEOPOLYMERIC MATERIALS BASED ON HALLOYSITE CLAY NANOTUBES

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In recent years, geopolymers have highlighted their potential as restoration materials due to their high workability and excellent thixotropic behavior, making them easy to spread and shape on various substrates commonly used in restoration work. Nevertheless, this study introduces innovative methods for creating eco-friendly composite geopolymers to explore new areas of application for these materials besides the construction field. For this purpose, natural nanoclays, particularly halloysite clay nanotubes (HNTs), in combination with cellulose sourced from Posidonia Oceanica sea balls were employed. Initially, our focus was on producing hybrid films using HNTs and cellulose from marine waste. By adjusting the HNT content from 30 to 80 wt%, we achieved composite films with properties similar to pure cellulose, even with a high clay concentration. SEM analysis revealed the formation of HNT aggregates within the cellulose matrix, impacting the films' microstructure and wettability. These films exhibited competitive elasticity and mechanical strength, demonstrating potential for packaging applications. Moreover, we transformed these films into geopolymeric materials through alkaline activation, resulting in significant improvements in tensile strength and suggesting their suitability for construction purposes. Furthermore, we propose an alternative approach for creating halloysite-based composite geopolymers by incorporating beeswax microparticles from Pickering emulsions. Characterization techniques confirmed the uniform dispersion of microwax particles within the geopolymeric structure, enhancing mechanical properties and heat storage capacity. These innovative methods represent a significant advancement in the development of sustainable composite materials, offering promising prospects for packaging and construction applications while addressing environmental concerns through the utilization of natural resources and waste valorization.

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MARBLE SCRAPS IN ECO-FRIENDLY MORTARS

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The large production of quarry scraps waste resulting from the cutting processes of ornamental rocks represents a significant environmental emergency due to its impact on air and aquatic eco-systems. This study investigates the use of various types of marble scraps from two important quarrying districts, as substitutes for traditional aggregates in the production of eco-mortars for building construction.

Sawing scarps from the white Carrara marble quarries and the "Orosei Biancone Tirreno" extractive district were selected in this study. These materials underwent phisico-chemical and microstructural characterization using OM, XRD, XRF, SEM, MIP and grain size distribution analysis. To assess the total replacement of traditional aggregates (standard sand UNI 196-1) with marble scraps, different white cement-based mortars (CEM I 52,5; UNI EN 197-1) were prepared. In three different mortars systems the binder content, with a maximum of 30% by weight, was replaced by Argical M1000 commercial pozzolanic clays mixtures. Super-pozzolanic silica fume was added at 5% by weight of the total binder content. The scarps were sieved with an automatic grinder and the different passing fractions were selected and mixed to achieve a more continuous granulometric distribution. The basic parameters of the mix design were selected by evaluating the water/cement ratio, hyper-fluidizer content and mortars workability. At different curing-time, ultrasonic pulse speed and compressive strength measurements were carried out on mortars.

The aim of this study was to evaluate the effects of the microstructure on the physical-mechanical performance of mortars, using two different artificial scarps-aggregates. The analysis of the physical-mechanical properties of the hardened mortars, revealed that the microstructural features of the scraps have a significant influence on the final properties. The partial substitution of cement binder with a pozzolanic agent can provide a more cost-effective solution without significantly reducing the mechanical strength of the mortar. Improved strength is achieved through interfacial adhesion forces on rough and more compact aggregates with few grain edges. The addition of both acrylic-based hyper plasticizer and pozzolanic additives enhance the mechanical performance, even when using waste scraps of granoblastic origin.

The incorporation of large amount of marble waste into white cement-based mortars, results in materials with good mechanical performance and high aesthetic value. This is an encouraging step in the design of mortars formulations for multiple purpose application (e.g., plasters, slurries for 3D additive printing and massive blocks/slabs for automatic machine processing), contributing to sustainability and reducing environmental impacts of the waste scarps.

PLA ELECTROSPUN MATS WITH ANTIOXIDANT ACTIVITY FOR FOOD PACKAGING APPLICATIONS

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The food industry is increasingly interested in new packaging technologies and natural compounds to extend product shelf life and preserve sensory characteristics. Active packaging, particularly those with antioxidant properties, is gaining attention for its ability to slow down oxidation processes responsible for food degradation. Electrospinning technology is gaining popularity in producing safe packaging materials for food applications, allowing the incorporation of active substances into microfibers to create materials with high porosity and a high surface-to-volume ratio. This study aims to develop and characterize novel active and biodegradable materials for food packaging by integrating electrospinning technology with natural antioxidant agents.

This study focuses on developing an active and biodegradable packaging using electrospinning technique, with polylactic acid (PLA) as the biopolymeric matrix and a commercial sample of bamboo leaf extract (BLE) as the antioxidant. The electrospun mats were produced using different BLE contents (10 wt%, 20 wt%, 30 wt%, and 40 wt%) and characterized by their morphology, mechanical properties, wettability, and antioxidant activity.

Scanning electron microscopy (SEM) micrographs showed that the presence of BLE influenced the fiber morphology, causing a slight increase in diameter in the PLA/BLE 10% and 20% systems and a slight reduction in fiber diameter in the PLA/BLE 30% and 40% systems in comparison with the neat matrix. Mechanical tests demonstrated that the addition of BLE concurrently decreased the modulus, maximum stress, and elongation at break compared to pure PLA. Wettability tests revealed that the addition of BLE led to an increase in hydrophilicity proportional to the amount of BLE added to the system. The amount of polyphenols present in the electrospun system increased proportionally to the content of BLE introduced into the material.

The addition of BLE to PLA can significantly alter the processability of the polymer matrix. The preliminary study concluded that the maximum BLE concentration incorporable into PLA is 40% by weight. This study confirms the feasibility of producing active and biodegradable electrospun mats containing high concentrations of natural antioxidant compounds potentially applicable in the field of food packaging.

BIOACTIVE WOUND DRESSINGS BASED ON POLYMER NANOFIBERS FABRICATED BY ELECTROSPINNING

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Advances in wound dressings relies on the development of novel materials that are able to revolutionize traditional approaches, offering more effective and personalized wound care. Electrospun nanofibers have been widely used recently as wound-healing dressings. Nanofibers have high porosity and good biocompatibility, promoting cellular respiration and regeneration of damaged skin. In addition, nanofibers can encapsulate active substances, such as hyaluronic acid (HA), which accelerates the healing process by regulating inflammatory responses, improving angiogenesis and collagen deposition at the wound site, and reducing scar formation. Here, we investigate the fabrication of HA-containing polyvinyl alcohol (PVA) nanofibers using the electrospinning technique. To enhance the stability of the PVA/HA nanofibers in aqueous environment, and avoid fast dissolution during wound healing, crosslinking by citric acid (CA) is studied.

Polymer solutions for electrospinning were prepared by dissolving PVA, HA and CA in ultrapure water in appropriate ratios. The process parameters were optimized in terms of applied voltage, flow rate, collecting distance and needle size. The obtained nanofibers were heat-treated at 150 °C to activate crosslinking by CA. FTIR was used to characterize the chemical composition and crosslinking of the samples. Morphology of the nanofiber mats was investigated by SEM, and thermal analysis by DSC was used to determine melting temperatures. To evaluate the potential application of the PVA-modified nanofibers for wound dressings, swelling and degradation tests were performed in PBS solution with different pH values (7–9).

PVA/HA/CA nanofibers were successfully prepared via solvent-free electrospinning. SEM analysis revealed that the fabricated fibers have diameters < 200 nm with a consistent size distribution across different samples. FTIR analysis confirmed crosslinking in the heat-treated PVA/HA/CA samples, and a decrease in melting temperature upon increase of the crosslinking time was determined by DSC. Swelling tests in PBS solution demonstrated that the heat-treated nanofibers are insoluble in water and that a correlation exists between the crosslinking time and the reduced dissolution of the samples. Finally, degradation tests in PBS confirmed the stability of the cross-linked nanofiber mats up to 48 h.

ELECTROSPUN TITANIUM DIOXIDE NANOFIBERS FOR BIOMEDICAL APPLICATION: PREPARATION, CHARACTERIZATION AND BIOLOGICAL INVESTIGATION

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Titanium dioxide (TiO_2) is attracting the attention in the biomedical field for its excellent properties such as stability, easy workability, low toxicity, great biocompatibility. Electrospinning is a simple and low-cost method employed to produce nanofibers exploited in several biomedical applications. The goal of this study is to turn a TiO_2 sol-gel solution into nanometric fibers by electrospinning process. The preparation, physical-chemical characterization and biological investigation of TiO_2 nanofibers are presented.

Titanium tetraisopropoxide (TTIP), polyvinylpyrrolidone (PVP), acetic acid is used to synthesize TiO_2 sol-gel solution in ethanol. A horizontal set-up is employed for the electrospinning of TiO_2 solution. The voltage, the flow rate and the distance are varied during the process. The obtained nanofibers are thermally treated at 400 °C to stabilize the anatase phase. Physical-chemical characterizations of nanofibers are carried out by means of SEM-EDS observations, XRD analyses, TGA evaluations. In vitro Alamar blue assay is assessed to investigate the cytocompatibility of the materials on MG-63 osteoblast cells after 24 hours and 72 hours.

SEM-EDS characterization proves the formation of defect free TiO_2 nanofibers with a mean diameter of (526 ± 86) nm. XRD analyses confirm the presence of mainly anatase phase and rutil. After calcination, nanofibers exhibit lower mean diameter (256 ± 54) nm due to the removal of polyvinylpyrrolidone at 200-300 °C as demonstrated by TGA results. Preliminary biological investigations reveal that the electrospun TiO_2 nanofibers are not consider cytotoxic for osteoblast cells at both considered time points.

In this study, the optimization of both synthetic conditions of TiO_2 sol-gel solution (PVP concentration) and parameters of electrospinning process lead to the formation of TiO_2 nanofibers. Therefore, the SEM-EDS observations highlight that the obtained electrospun TiO_2 nanofibers show an adequate morphology, with no defects, as well as homogeneous distribution. Since the anatase crystalline phase seems to promote the cell growth better than the amorphous one, the calcination process plays a key role to achieve pure anatase TiO_2 nanofibers as pointed out by XRD characterization. TGA analysis also corroborates that the thermal treatment is required to remove the polyvinylpyrrolidone. Furthermore, the in vitro biological evaluation supports the citocompatibility of TiO_2 nanofibers for osteoblast cells. Even if further studies are needed concerning the osseointegration and the interaction of TiO_2 nanofibers with the surrounding tissues, the herein combination of sol-gel approach and electrospinning process represents a powerful tool to easily obtain ceramic nanofibers for biomedical application.

AN INNOVATIVE AND SUSTAINABLE ROUTE TO PRODUCE MgO NANOPARTICLES TO BE USED IN CANCER THERAPY

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The intrinsic features of MgO nanoparticles-MO NPs-in terms of antibacterial agent and cytotoxic behaviour towards cancer cells has become the intriguing challenge, introducing a new criterion for the development of extensive applications of NPs in medical field. Most of current synthetic routes for NPs production are not able to satisfy the global challenge in terms of sustainability, green approach and scalability, being characterized by drawbacks such as high temperature/pressure conditions, expensive/sophisticated apparatus, long synthesis times and low yield of production. The possibility provided by our innovative and sustainable ion exchange synthetic route to produce in only 15 minutes up to almost 10 kg/week of pure and crystalline $Mg(OH)_2$ NPs-MH NPs-useful as precursor to MO ones, can constitute an important goal to define the starting point for the scale-up in the NPs production to market requests.

We firstly synthesized an aqueous suspension of MH, used as precursor, that was dried at 110°C for 24 hours and then calcinated at 500° C for 4 hours, so obtaining MO NPs. Phase purity, crystallinity and particles morphology of both MH and MO were analysed by using XRD and TEM/HRTEM techniques. The MO powders were dispersed in a PBS solution, giving rise to different MO suspension concentrations that have been injected into a culture of melanoma cells. After 24, 48 and 72 hours of treatment a viable count was carried out, the number of live cells at the different incubation times was established, and the growth curves were determined. Finally, the evaluation of the influence of MO NPs on human skin fibroblasts (HS27) were investigated too.

Pure and crystalline MO NPs were produced, having BET values up to 137 m^2/g. The NPs appeared organized as a network of intercrystallite channels, preserving the original pseudo hexagonal-platelet morphology of the precursor, and formed by an aggregation of monodispersed-roughly spherical NPs < 10 nm. When the MO NPs were added to melanoma cells, a clear cytotoxic effect was detected already at low incubation times and low MO suspension concentrations, giving rise to a non-negligible reduction of cellular proliferation. After 72 hours, by increasing the MO concentration, a reduction of the cellular activity up to an order of magnitude was observed. When the highest MO concentration was reached, a total inhibition of the cell growth was detected, with a number of live cells almost constant during the whole incubation time. The results coming from the skin fibroblasts (HS27) showed as the MO NPs did not alter both vitality and proliferation of healthy cells.

NEW OPPORTUNITIES FOR IMMUNOTHERAPY: CRAFTING LARGE-PORE MESOPOROUS SILICA NANOSTRUCTURES AND NANOSTRUCTURED LIPID NANOPARTICLES

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Genetically engineered T cells-based immunotherapy has shown remarkable success in clinical trials. Key for the emergence of gene-modified cell therapies, especially T cell therapies, are lenti- or retroviral vectors. Although the current approaches utilizing retro- or lentiviral vectors are efficient, they come with a relatively high cost. Additionally, despite the implementation of several safety mechanisms, they are not completely devoid of residual risks such as germline transmission, immunogenicity, and insertional mutagenesis.

Consequently, there is a quest for the development of efficient strategies enabling non-viral transduction of synthetic receptors into primary T cells. Here, synthetic nanovectors, in combination with a specific plasmid (pSLCAR-CD19-28z), were designed. This approach aims to circumvent chromosomal integration and mitigate the risks associated with insertional mutagenesis. Specifically, Nanostructured Lipid Carriers (NLCs) along with two variants of mesoporous silica nanoparticles (MSNs) featuring large pores, namely core@shell nanostructures (SiO_2@MSNs) and hollow MSNs (H-MSNs), were synthesized. These synthetic nanovectors were selected for their numerous advantageous properties, including a high degree of biocompatibility, biodegradability, ease of preparation, and efficient loading capacity for therapeutic agents.

NLCs were fabricated through hot homogenization and subsequently loaded with the plasmid using a hydrophobic ion pairing approach. SiO_2@MSNs and H-MSNs were synthesized employing a dynamic soft-templating strategy and a single-step sol-gel process, respectively. Following synthesis, both silica-based nanostructures were surface-functionalized with a cationic polymer (polyethyleneimine, PEI) as an initial step for loading the pSLCAR-CD19-28z plasmid.

The pSLCAR-CD19-28z plasmid was loaded into NLCs via complexation with a cationic lipid, ensuring its encapsulation within the hydrophobic lipid core. PEI-decorated SiO_2@MSNs, featuring a dahlia-like morphology with a non-porous silica core and a dendritic mesoporous silica shell, as well as H-MSNs, were characterized by large pore diameters of up to 30 nm. Both the MSNs and NLCs demonstrated an average hydrodynamic diameter below 200 nm and also displayed considerable colloidal stability in physiological media. They were capable of releasing the plasmid while preventing its degradation.

The thorough chemical-physical characterization, combined with in vitro studies, confirmed these nanostructures as promising candidates for immunotherapy.

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DEVELOPMENT OF ACID-FREE CHITOSAN FILMS IN FOOD COATING APPLICATIONS: PROVOLONE CHEESE AS A CASE STUDY

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Chitosan has been extensively explored in food coatings. Still, its practical application is largely hampered by its conventional wet processing in acetic acid, whose residuals negatively impact food quality and safety. We propose a new method to formulate chitosan coatings for food applications by avoiding organic acid processing and validate them on a cheese model.

The procedure entails modifying a previously reported process based on HCl chitosan treatment and neutralising the resulting gel. The obtained chitosan is solubilised in water using carbonic acid that forms in situ by dissolving carbon dioxide gas. The reversibility of water carbonation allows for easy removal of carbonic acid residues, resulting in acid-free chitosan films and coatings. We characterised the chitosan solutions (rheology) and the derived films' properties (water stability, barrier and optical properties). Then, we assessed the performance of the coating on Provolone cheese as a food model (mass transfer and texture profiles over 14 days). In addition, the migration of acetic acid into the food matrix that occurs in conventional chitosan coatings was measured.

Viscosity measurement showed a strong shear thinning behaviour of chitosan solutions in carbonic acid, facilitating the coating processes. The acid-free chitosan films have superior water stability and barrier properties compared to commonly acetic acid ones. When applied to Provolone cheese, acid-free chitosan coatings showed the ability to preserve cheese properties comparable to commercial PVAc and chitosan film from conventional aqueous acetic acid. Still, it was demonstrated that the residual acid in acetic acid-processed chitosan exceeded the specific migration limit for packaging in contact with food and the odour detection limit.

In conclusion, processing chitosan via wet approaches that eliminate acetic acid has been proven to be a promising alternative to conventional dissolution. This method further enhances the properties of chitosan films. It enables them to meet stringent food quality requirements and safety regulations, paving the way for an effective application of chitosan in future food contact applications.

PHOTOSTABLE AND BIOCOMPATIBLE CARBON DOTS FROM CITRIC ACID FOR BIOIMAGING

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The article discusses the use of Carbon Dots (C-dots) for bioimaging. C-dots are nanoparticles that require low-cost, highly emissive, and photostable systems with low cytotoxicity. In this work, two C-dots were synthesized from citric acid and tris(hydroxymethyl)aminomethane (CATris) or arginine methyl ester dihydrochloride (CAArg).

Structural and optical properties were analyzed by UV-Vis, Infrared, DLS, ζ-potential and spectrofluorimetric measurements. The photostability was assessed through exposure to UV light and measure of fluorescence intensities. Cellular uptake and bioimaging were tested in vitro using murine neuroblastoma cells and ovine fibroblast cells.

The C-dots are highly biocompatible, and after 24 hours of incubation with the cells, a vitality of 100% was still observed. In addition, the C-dots synthesized using tris have an average size of 2 nm, a quantum yield of 37%, high photostability, and a ζ-potential around -12 mV.

Citric acid represented a common source to form a carbonaceous core of the dots, while tris (hydroxymethyl) aminomethane was chosen for the possible formation of a dendritic structure of the carbon dot surface and has been reported to be the source of its great stability. Arginine, instead, has a guanidinium group that is characterized by stronger interactions with the cell membranes, thus providing an efficient uptake. Both C-dots species display absorption bands in the UV interval and blue emissions arising from the carbonization of N-source precursors. In accordance with the literature, photostability has been evaluated by considering the fluorescence emission intensity during lengthy continuous excitation. The high photostability exhibited by CATris is very important because, despite the versatility of organic dyes in the staining of living and fixed cells, their susceptibility to photobleaching represents an inherent problem that limits the applications of organic dyes in cell imaging for long durations. The nanometric dimensions and ζ-potential around −12 mV enables the C-dots to be attracted to cell membranes efficiently and to evenly dislocate inside the cells without damaging them and allowing for very effective bioimaging.

POORLY CRYSTALLINE IRON OXYHYDROXIDES NANOPOWDERS AS SORBENTS FOR ARSENIC REMOVAL FROM WATER

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Arsenic pollution in surface water and groundwater is a worldwide problem due to its natural abundance due to dissolution from soil or anthropogenic activities. Due to the formation of inner-sphere complexes, the high surface-to-volume ratio and, therefore, the high density of active sites (-OH groups), nanopowders of iron oxides and oxyhydroxides show a high affinity for arsenate and arsenite species in wide pH ranges and pollutant concentrations, which is particularly promising also due to their low production costs and low toxicity. In this work, the removal of arsenic from water by poorly crystalline nano-oxyhydroxides (akaganeite, ferrihydrite and feroxyhyte) was studied by adsorption batch experiments together with a detailed characterization of the surface, textural and morphological properties.

Akaganeite (β-FeOOH), ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$), and feroxyhyte (δ-FeOOH) were synthesized by simple precipitation methods and tested for the removal of arsenic from water by changing different parameters, such as initial concentration, contact time, ionic strength, presence of competing ions and solid to liquid ratio. The same experimental conditions for the batch tests allowed a direct comparison between the adsorbents. All sorbents were characterized by X-ray Diffraction (XRD), Transmission electron microscopy (TEM and HRTEM), N_2-physisorption, electrophoretic light scattering (ELS), thermogravimetric-analysis (TGA), and Fourier-transform infrared spectroscopy (ATR-FTIR).

Thanks to its high and positive surface charge, akaganeite was found to be the most promising sorbent in the whole pH range for As(V) (qe = 89 mg/g at pH 3 and 52 mg/g at pH 8 for CAs = 500 mg/L) and to keep good removal ability also for As(III) (91 mg/g at 500 mg/L, pH 3 and pH 8), whose best sorbent was ferrihydrite (144 mg/g at 500 mg/L and pH 8), due to the high surface area. Preliminary results on feroxyhyte proved its suitability as sorbent for As(V) (38 mg/g at 100 mg/L and pH 3) as a promising alternative to akageneite (41 mg/g at 100 mg/L and pH 3). Other removal tests were carried out on the best adsorbent, i.e. akaganeite, to investigate the effect of the initial As concentration, contact time, ionic strength, and the presence of competitors.

2nd POSTER SESSION

3D-PRINTED SOFT MAGNETIC COMPOSITES FOR BRUSHLESS MOTORS IN SPACE COLONIZATION APPLICATIONS

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Among the several criticalities for future space exploration and colonization is undoubtedly the supply of raw materials to manufacture every component needed. The utilization of the resources presents on the surface of a moon/planet, as well as secondary raw materials extracted from end-of-life components, represents the only sustainable solution for long-term Out-of-Earth permanence. Moreover, Additive Manufacturing is a new paradigm of manufacturing with unrivalled freedom of geometry and equipment flexibility, which is ideal for the requirements of space exploration. Magnetic materials are key components in many devices aboard any spacecraft, such as motors, mechanisms, actuators and sensors. The possibility of manufacturing magnetic components with materials available in situ and through techniques employable in space and on a celestial body is a valuable perspective for the future of space agencies.

In this work, funded by the European Space Agency (contract 4000136889/21/NL/GLC/ov), composite and nanocomposite materials with soft magnetic fillers from materials available on the Moon and processable via Fused Filament Fabrication 3D printing were developed.

Polyether-ether-ketone (PEEK), a high-performance thermoplastic polymer, was chosen as matrix and three different fillers, namely magnetite, nickel-zinc ferrite and FeNi alloy, were selected. Several compositions, from 50 to 85 wt% of filler content. The raw materials were compounded, extruded into filaments and successfully 3D printed via FFF technique into test samples and technology demonstrators.

Mechanical, thermal and electromagnetic numerical simulations were performed to design an optimized brushless motor for space applications employing the developed materials as stator core.

All formulations showed thermal and mechanical properties typical of a high-performance polymer composite, with thermal stability up to 600°C, glass transition always above 150°C, high rigidity and retention of mechanical properties at high temperatures, although a reduction in ductility was recorded. The magnetic characterization revealed coercivity, remanence and saturation magnetization values which are very promising for the use in brushless motor components. Simulations with the better performing composition (85% FeNi) showed achievable torque values compatible with low power applications such as micro-actuators, pointing devices for small antennas and gyroscopes, demonstrating the feasibility of the applications of the developed materials. Finally, a prototype demonstrator of the motor stator was 3D-printed with the best material.

DEVELOPMENT OF GRAPHENE-BASED ANTI-CORROSIVE COATINGS FOR HYDROGEN TRANSPORT NETWORKS

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The supply of hydrogen can take place through current gas distribution networks however the diffusion of hydrogen inside the steel pipes leads to the onset of embrittlement phenomena. The use of graphene coatings as a barrier layer to limit hydrogen embrittlement appears promising. The techniques used so far in the literature to deposit graphene on metal substrates appear too expensive to be applied on a large scale. The present objective is to obtain graphene coatings using low-cost and easily implementable techniques such as electrochemical deposition.

The samples are obtained from a pipeline made of API X65 steel. Two mixtures are tested, one containing graphene oxide (obtained by the modified Hummers method) and one containing suspended graphene flakes (produced through a low environmental impact process that involves the dispersion of graphite powder into a mixture of isopropyl alcohol and ultrapure water and sonicated in an ultrasonic bath). The samples are brought to different surface roughness and cleaned in the acetone bath before deposition. The tests are carried out imposing an anodic current on the metal. The deposits obtained are characterized by microscopic observations (optical, SEM and AFM).

The deposits obtained from the graphene oxide solution cover the sample uniformly and homogeneously. A current of 0.6 mA/cm2 for 8 minutes corresponds to a deposit thickness of 10 microns that shows good surface adhesion. The deposit thickness was found to be a function of current density and deposition time; the adhesion capacity between graphene and substrate depends also on the surface roughness of the latter. Conversely, the deposits obtained from the graphene suspension only partially cover the surface of the samples and do not appear homogeneous regardless of the applied potential or the set current.

The electrochemical deposition of graphene oxide is based on two steps. The charged graphene oxide flakes move for electrophoresis toward the oppositely charged electrode driven by the electric force, subsequently, the deposition process occurs on the electrode surface where the graphene flakes are accumulated. For this reason, the un-charged graphene flakes did not produce a uniform deposit. Some tests of in-situ oxidation of graphene are in progress. The ability of these deposits to decrease the passage of hydrogen in steel will be further evaluated by permeation tests.

INVESTIGATING ISOTHERMAL ANNEALING EFFECTS ON NANOPOROUS GOLD LIGAMENT MORPHOLOGY

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Nanoporous gold (NPG) films demonstrated significant potential across a diverse spectrum of applications, including catalysis, electrochemical sensing, biotechnological innovations, mechanical actuation, thermal management, and filtration systems. The operational efficiency of NPG in these applications is critically dependent on its thermal stability. Indeed, when exposed to temperatures beyond a specific limit, NPG undergoes a coarsening process that progressively alters its structural and functional attributes. For this reason, in the present work, the evolution of the microstructure of NPG as a function of temperature has been studied.

By dealloying an $Au_{20}Cu_{48}Ag_7Pd_5Si_{20}$ master alloy, NPG samples were prepared and subsequently examined using serial block-face scanning electron microscopy (SBF-SEM) after embedding in epoxy and gold sputtering. The morphological changes during isothermal annealing at 550, 580, and 630°C were studied, focusing on the behavior of the ligaments under varied thermal conditions.

Annealing at 550°C and 580°C preserved the NPG structure, whereas 630°C induced significant morphological alterations, manifesting as densification and a deviation from the material's characteristic topology. Ligament evolution displayed heterogeneity, including thickening, maintaining size, thinning, fluctuating, and undergoing pinch-off events. The observed variations, albeit diverse, suggested that surface diffusion is the primary mechanism driving the coarsening process, as evidenced by the linear relation between the time and the adjusted fourth power of ligament thickness.

This investigation shows the intricate relationship between thermal exposure and NPG morphology, highlighting thermal management's crucial role in preserving material integrity for precise applications. The distinct morphological transformations at 630 °C, governed by surface diffusion, provide insights into optimizing NPG's thermal stability for advanced applications.

ADVANCEMENTS IN RESIDUAL STRESS ANALYSIS VIA ION BEAM MICROSCOPY: NEW PERSPECTIVES AND HIGH-RESOLUTION PROTOCOLS FOR INDUSTRY

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The Focused Ion Beam-Digital Image Correlation (FIB-DIC) ring core method has become pivotal in addressing industrial challenges related to residual stresses, crucial for the effective design of components. Its localized nature allows precise investigation of stresses in areas of interest within complex microstructural challenges. This technique's recent advancements, achieving sub-50 nm resolution (in the context of the European nanoMECommons project), are instrumental in advancing the understanding of residual stresses in novel 3D printing processes and micro-electromechanical actuators in micro-electronics. The ability to accurately measure and analyze these stresses is vital for optimizing component designs and enhancing the reliability of advanced manufacturing technologies.

Hereby, we propose a collection of relevant state-of-art applications to elucidate the advancement in the field of localized stress measurement. The main advancement is represented by a multi-area approach in tracking surface induced relaxations that enhances the in-depth resolution while maintaining maximum sensitivity during integration method application between steps. It focused on PVD-deposited CrMnFeCoNi and CrMnFeCoNiN multilayered coatings with 50 nm and 200 nm layer thicknesses (coupled with high-resolution nano- x-ray diffraction), multi-layered MEMS devices, and super duplex stainless steel samples produced via Laser Powder Bed Fusion (LPBF).

The 200/200 nm multilayer analysis revealed calculated stresses of -0.10 GPa ± 0.05 in the first CrMnFeCoNiN layer and -0.8 GPa ± 0.05 in the first CrMnFeCoNi layer, showing, for the first time, the ability to track jumps in stresses related to interfaces in multilayered PVD systems (in precise agreement with nano-diffraction measurements. In MEMS devices we demonstrate the capabilities of measuring stresses varying across micro-cantilever specimens (from the campings to the center of double-clamped cantilevers) with variations, respectively, from 300 MPa to 60 MPa. The 3D-printed super duplex stainless steel exhibited positive relaxation strain values (compressive residual stresses), which decreased by approximately 30% following annealing at 300°C for 4 hours, suggesting stress inducement via production or mechanical surface finishing processes.

This study emphasizes the FIB-DIC ring core method's enhanced ability to analyze residual stresses with high resolution and sensitivity across various materials and manufacturing processes. It highlights the method's critical role in identifying stress distributions that are key to optimizing material properties and advancing stress measurement technologies, thereby supporting the development of more reliable and effective components in industrial applications.

UNVEILING HIDDEN PRINTS: OPTICALLY STIMULATED LUMINESCENCE FOR LATENT FINGERPRINT DETECTION

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Traditional methods of detecting latent fingerprints using fluorescent lighting and optical techniques often face limitations, particularly when dealing with surfaces that exhibit luminescence. As a result, fingerprint evidence can go undetected or be overlooked due to inadequate detection and limited detail. In this study, we propose the utilization of optically stimulated luminescence (OSL) applied to a Ba_2SiO_4 matrix co-doped with Eu^{2+} and Dy^{3+} as an innovative approach to visualize latent fingerprints on various surfaces, including thin plastic bags, rigid duct tape, thin aluminum foil, and glass slices. By effectively eliminating any luminescent background, this technique significantly enhances optical imaging, addressing the shortcomings of traditional methods. This study marks the first successful application of OSL in the development of latent fingerprints, offering promising prospects for more efficient and effective forensic techniques in the future.

The synthesis of Ba_2SiO_4 phosphor powders involved a solid-state reaction method, with doping concentrations of 0.5 mol% Eu and 0.2 mol% Dy. Precursors including $BaCO_3$, SiO_2, Eu_2O_3, Dy_2O_3, and BaF2 as a flux were mixed and heated in a tubular furnace at 1000°C for 6 hours. Subsequently, the powder underwent a reduction process at 1250°C for 4 hours in a reductive atmosphere to convert Eu^{3+} to Eu^{2+}. After annealing and sieving, the Ba_2SiO_4 powder was prepared for use.

Latent fingerprints were deposited after thorough hand washing, where a donor rubbed their forehead and pressed their finger onto a substrate. Ba_2SiO_4 powder was applied using a fiberglass filament brush, with and without prior cyanoacrylate application.

The results showed the potential of the optically stimulated luminescence (OSL) method in developing clear and concise fingerprints.

This study proposes a powerful method for visualizing latent fingerprints by employing OSL on a Ba_2SiO_4 matrix co-doped with Eu^{2+} and Dy^{3+}. Fully characterization from structural (XRD, Raman, SEM) and optical characterization (PL, TRPL, PLE) have performed on different phosphor crystals. The application of OSL successfully overcomes the challenges posed by luminescent backgrounds and greatly improves optical imaging. The versatility of this technique is demonstrated through its successful detection of latent fingerprints on various surfaces, including thin plastic bags, rigid duct tape, thin aluminum foil, and glass slices. This research marks the first successful application of OSL in the development of latent fingerprints, representing a significant milestone in forensic science. The findings pave the way for the future development and implementation of more efficient and effective forensic techniques.

RECYCLING OF THERMOPLASTIC POLYURETHANE USED IN BINDER JET 3D PRINTER

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The Binder Jet (BJ) 3D printing technology, industrially used for medium and large-scale productions, allows the limitations of traditional manufacturing to be overcome by reducing startup costs and obtaining already functional prototypes. Material printed with BJ technology already involves recycling unused powder during printing, up to 80%, but there is no recycling planned for the printed material. The proposed work focuses on presenting the mechanical properties of specimens printed using BJ technology after several printing cycles of the thermoplastic polyurethane (TPU).

The thermoplastic polyurethane (TPU) recovered for 70% every BJ printing process is referred as Recycling Printing, (P_TPU) mixed with 30% of Virgin or unused TPU (V_TPU) during each printing process. The mechanical properties of BJ-printed specimens are compared with those specimens obtained through compression moulding (CM) and composed of 70% P_TPU and 30% V_TPU. The use of CM serves as a model for contemplating the application of P_TPU, either in isolation or mixed with varying percentages of V_TPU.

The study of the mechanical properties is extended to the specimens produced using the recycled powder derived from BJ 3D printed artefacts that undergo a mechanical recycling process (referred to as Artefact Recycling, A_TPU) in a circular economy perspective.

Preliminary results of tensile tests highlight higher values of elastic modulus, elongation at break, and strength of specimens produced by CM, respectively around 137 MPa, 16 MPa and 330% than BJ technique of about 104 MPa, 10 MPa and 86%, respectively. On the other hands, the A_TPU speciments by CM show a significative decrease of the mechanical properties respectively around 66 MPa, 9.3 MPa and 29% highlighting the contribute of the binder agents. Comparative results from different processing and TPU materials will be also presented.

Studying the evolution of the mechanical properties of the TPU recycled powder at each printing process allows the optimisation of BJ 3D printing. Indeed, P_TPU shows a decrease in the mechanical properties at each recycling process during BJ 3D printing. In contrast, P_TPU samples produced by CM process show higher mechanical performance at the same recycling of BJ printing suggesting a different application for the P_TPU when it considered as waste in BJ process. The recycling method and the process were optimized in order to obtain mechanical properties suitable for different applications.

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ADVANCED COMBINATORIAL APPROACH TO ASSESS PROCESSING AND ENVIRONMENTAL DAMAGE IN TITANIUM THIN FOILS

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When Ti is employed for laminated components with structural functions, despite their high structural performance, it is necessary to assess various mechanical aspects, including the residual stresses induced by the lamination process. Moreover, if these components operate in aggressive hydrogen-rich environments, there might be further performance loss due to the formation of hydride phases, leading to embrittlement. Addressing this in a fast industrializable protocol is vital for sustainable, efficient processes within a circular, green economy, balancing durability against environmental impact.

Our focus was on a correlative multi-technique approach of bicomponent Ti/Al foils in which the Ti represents the structural element and the Al acts as a heat dissipative component during the operation, assisting Ti to maintain its stability. We used the sin^2ψ analysis technique using XRD for the residual stress evaluation within crystalline materials. To detect, quantify, and characterize hydride phases within the foils we used different techniques, the first SAD TEM analyses, initially identified and described the microstructure of various hydrides as a function of the working conditions. This was followed by semi-quantitative XRD to confirm the hydride concentrations and phases. An innovative approach is then studied to mechanically quantify hydride concentrations and mechanical properties utilizing high-speed nanoindentation mapping coupled with machine learning deconvolution protocols, leveraging the mechanical anisotropy due to hydride formation.

We found that Bi-axial residual compressive stresses characterize all samples. The significant difference is in the intensity which is around -1000 MPa along the parallel direction to lamination, compared to the normal lamination direction, characterized by average values around -4000 MPa. Two species of hydrides were identified in the analyzed samples: firstly, Ti_2H, which exhibits a tetragonal face-centered crystal lattice, primarily concentrated at the edges of the foil, mainly formed due to interstitial inclusions produced by hydrogen migration within the Ti crystal lattice, causing lattice distortion. Secondly, TiH_2, which instead presents a face-centered cubic crystal lattice was detected at the center of the foil with an average concentration of 15% in all analyzed samples.

Being a ceramic phase, it is the main cause of hydrogen-induced embrittlement. The difference in concentration was mainly attributed to the shielding effect produced by the foil's grips against hydrogen contamination. The third analytical technique employed utilizes the anisotropy of modulus and hardness properties, particularly the latter, induced by the formation of titanium hydrides, validating a non-destructive automated method for identifying and estimating hydrides present.

INFLUENCE OF PRODUCTION SYSTEMS AND ANODIZING TREATMENTS ON ADDITIVELY MANUFACTURED MECHANICAL INTERLOCKING STRUCTURES

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Multi-materials are attracting increasing interest in today industries as a means of producing highly functional and lightweight components. As they become more widely used in engineering applications, especially in the automotive and aerospace sector, metal-composite components are of particular interest. Effectively joining these materials can be challenging due to their fundamentally different chemical composition and mechanical properties. A recent development in joining techniques involves the use of mechanical interlocking structures, which are arrays of protrusions formed on the surface of one of the two materials to be joined. By exploiting the geometries of these structures and their roughness, the second material to be joined can be locked to the first one, without the need for additional joining methods, such as adhesives or fasteners. Additive manufacturing can be used to produce interlocking structures due to its unique ability to build complex shapes, resulting in a single-step manufacturing process that reduces both cost and time.

At first, particular attention was paid to the design phase of the interlocking structures. Afterwards, AlSi10Mg substrates with interlocking structures were manufactured using the powder bed fusion technique, using a laser beam as energy source (PBF-LB). Two different PBF-LB systems were used, and the samples produced were compared by means of metallographic characterizations. Finally, different electrochemical treatments and bath conditions were investigated to evaluate the feasibility and the effects of performing an anodizing process on the 3D metal surfaces.

An arrow-shaped geometry was chosen after an extensive literature review. Both PBF-LB systems were able to produce the geometry, but one system achieved better geometry accuracy. The morphology and properties of the anodic layer on the different areas of the PBF-LB samples were analyzed and correlated with the anodizing process parameters.

The metallographic characterization of the samples suggested that there is a strict correlation between the geometrical accuracy of the interlocking structures and the PBF-LB building conditions. Therefore, particular attention should be given to these aspects. In addition, anodizing surface treatments on the metal surface could be performed, highlighting the difficulty of developing an oxide layer on a 3D surface of complex shape.

3D-PRINTABLE COMPOSITE MATERIALS AS SUSTAINABLE ALTERNATIVES TO LEATHER FOR THE UPCYCLING OF LEATHER WASTE

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Leather industry has a notable environmental impact due to the tanning process. Additionally, around 30% of finished leather is wasted in manufacturing. Bio-based alternatives to leather employing diverse materials, including the ones derived from bacterial fermentation, mitigate the ecological footprint of genuine and synthetic upholstery material. Besides, the evolution of 3D printing has fostered consumer expectations for personalized products. This research aims to valorize leather waste by developing a circular, 3D printable and composite material alternative to leather.

Bacterial cellulose was produced through fermentation of Kombucha tea. The composite material matrix included gelatin, hydrolyzed bacterial cellulose with H_2SO_4 30%(v/v), and glycerol as a plasticizer. Grinded leather waste (granulometry<0.5 mm) served as filler and was added from 10 to 20% with respect to the matrix dry weight. Various compositions of the matrix components were examined. Mechanical properties of dried composite materials were analyzed through uniaxial tensile tests. Rheological characterization of the circular materials in the wet state was conducted through oscillatory and flow tests. The Direct Ink Writing 3D printing technique was employed for shape fidelity assessments.

Tensile tests showed values of ultimate strength, elongation at break and elastic modulus of the same magnitude of original state leather. Rheological analysis demonstrated a shear-thinning behavior. Moreover, thixotropy tests demonstrated a recovery after high-amplitude deformations. The 3D printed grids and coils exhibited filament uniformity with an extremely low spreading, and the shape fidelity indexes were in accordance with the desired ones.

Tensile tests showed that gelatin content enhanced the mechanical strength, while the increasing of leather powder content in the composite material did not notably effect mechanical properties. Rheological flow tests showed materials suitability for extrusion-based printing, owing to their pseudo-plastic behavior. Thixotropy tests demonstrated the materials ability to recover after the extrusion process through the nozzle. This result was validated by printability tests, which revealed the high shape fidelity of printed structures. In conclusion, the development of a 3D-printable composite material, derived from waste and biobased sources, represents a significant step towards sustainable strategies within a circular economy framework.

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SMART TEXTILE OF PVDF WITH MORPHING AND PIEZOELECTRIC PROPERTIES

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The use of smart materials in high-tech industries and material science technology is rapidly gathering significant interest. The use of these innovative materials has a remarkable advantage of providing unprecedented functionalities as their capabilities of being remotely actuated when exposed to external triggering sources. For instance, these materials can change their configuration, or alter their physical properties with the application of stimuli such as, electricity, magnetic field, etc.

In this work, a novel piezo-magnetic textile made of composite PVDF fibers with embedded magnetite microparticles, using a wet-spinning technique, is presented with particular focus on the implemented multi-scale process design and functional characterization.

The process consists of a multi-scale approach. First a wet-spinning process is implemented to realize single magnetic filaments of PVDF which are spontaneously polarized during manufacturing, and then to assemble such micro-scaled filaments to form a woven macroscopic textile. The wet-spinning process consists of a magnetite-based PVDF solution passing from a syringe to a coagulation bath. The solution was extruded and collected by a rotating drum.

The filaments were fully constrained at the two edges and actuated with a piezoceramic for dynamic characterization with the support of a scanning laser vibrometer with and without the application of a magnetic field. The piezoelectric response was studied by means of a pneumatic actuator, to impact the samples at various rates, in conjunction with an oscilloscope that was used to assess the acquired charges over time.

The PVDF/Magnetite filament was found to be characterized by a decrease in resonance frequency with respect to bare PVDF filaments. The application of a magnetic field instead induces an increase in resonance frequency as well as an increase in damping ratio of PVDF/Magnetite filament which was also found to be higher than that of the bare PVDF filament. The composite textile was also found to possess piezoelectric properties despite the simplicity and low processing costs.

This study shows the possibility of realizing functional textile with a low-cost approach. It is shown that the filament dynamic response (natural frequency and damping) is highly related to the application of a magnetic field that allows to modulate the material stiffness. In other words, and most importantly, the work highlights the possibility of fine-tuning the material design to reach the desired dynamic response (vibration and damping) while at the same time possessing piezoelectric properties, which can be used to provide additional functionalities to the textile.

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EFFICIENT VISIBLE-LIGHT-RESPONSIVE CORE-SHELL PHCN-TiO_2 PHOTOCATALYSTS FOR SIMULTANEOUS ORGANIC POLLUTANT REMOVAL AND HYDROGEN PRODUCTION

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The imperative for hydrogen (H_2) production technology arises from its role as a clean and versatile energy carrier, vital for decarbonizing various sectors and achieving a sustainable energy transition globally. Photocatalysis for H2 production involves utilizing semiconductors to absorb light and facilitate the splitting of water into hydrogen and oxygen. The challenge with H_2 generation is to ensure its cost-effectiveness, low carbon emissions and high efficiency. In this work, we synthesize novel Phenyl modified carbon nitride (PhCN) core - TiO_2 shell hybrid photocatalysts which show excellent H2 production capabilities under visible-light irradiation with the eradication of organic pollutants from water.

PhCN was prepared by a one-step, one-precursor process from phenyl-triazine followed by the growth of titania through a solvothermal route to form a heterojunctional organic-inorganic photocatalyst. Four hybrids were prepared with various mass ratios between the components. The hybrids were further treated at different annealing temperatures. The structural and optical properties of these materials were studied. The photocatalytic efficiencies of the hybrid series were evaluated under visible light irradiation for the degradation of rhodamine B, methylene blue and methyl orange dyes along with hydrogen evolution measurements in a homemade closed reactor system. The optimised photocatalyst was studied to produce H_2 simultaneously while degrading the dye.

The structural characterization techniques- (XRD, XPS, RAMAN, FTIR, spectroscopies) show the successful integration of the two components of the hybrid. The optical spectroscopy data (PL, TRPL, UV-Vis) ensures a successful charge-transfer between the components. The optimized hybrid shows a core-shell structure under electron microscope (EDS, TEM). It shows the kinetic constant for rhodamine B dye degradation to be $2.3\times10^{-2}min^{-1}$ and has a H_2 production activity of 6.3 $\mu mol\ h^{-1}\ mg^{-1}$ under visible-light illumination.

Both- the ratio between the two hybrid components and the annealing temperature play a vital role in determining morphology and properties of the material. Various properties prove to contribute to the effectiveness of a photocatalyst- crystallinity, surface area, porosity, absorption, morphology etc. The optimised hybrid shows great reproducibility and recyclability.

WARM WHITE LIGHT EMISSION FROM $Cs_2Na_{1-x}Ag_xIn_{1-y}Bi_yCl_6$ DOUBLE PEROVSKITE NANOPARTICLES

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Double perovskites $Cs_2Na_{1-x}Ag_xIn_{1-y}Bi_yCl_6$, shows interesting optical characteristics. Celebrated for emitting warm white light with nearly perfect quantum efficiency, rendering them exceptionally promising for solid-state lighting applications. The reproducibility of the emission spectrum, combined with the materials' resilience against degradation and their synthesis from eco-friendly, non-toxic precursors, enhances their attractiveness. However, the emission efficiency proves markedly sensitive to the materials' composition, with minor variations causing substantial fluctuations in the photoluminescence quantum yield.

Our investigation encompasses both bulk material and nanoparticles dispersed in solution. We utilized a comprehensive suite of measurements for characterization purposes. Synthesis of nanoparticles involved the incorporation of Bi and Ag at a minimal 0.1% fraction, a critical parameter for efficient warm white light emission. The alloying of Ag emerged as a significant factor in achieving high emission yields. Microscopic mechanisms were scrutinized through continuous-wave spectroscopy measurements and ab initio computations of the electronic band structure. Additionally, time-resolved photoluminescence and transient absorption spectroscopy were employed to study the roles of Ag and Bi in the formation of bright self-trapped excitons and inhibition of exciton relaxation.

Our findings revealed the pivotal role of Bi in enhancing optical absorption at the band gap edge of the double perovskites. The combination of Ag and Bi facilitated the formation of radiative self-trapped excitons, leading to elevated quantum yields. Notably, nanoparticles exhibited a high quantum yield, reaching approximately 34%, providing valuable insights into the interplay between composition and optical properties in double perovskite materials. Furthermore, synthesis utilizing holmium and other rare earth elements resulted in remarkably stable nanoparticles with adjustable emission.

The observed quantum yield efficiency, though not approaching unity, underscores the potential of nanoparticles in solid-state lighting applications. This nuanced understanding enriches our comprehension of the intricate relationship between composition and optical properties in double perovskite materials. The synthesis of nanoparticles incorporating rare earth elements like holmium highlights the versatility and stability of the resulting material, opening avenues for tailored optical applications. These insights pave the way for further exploration and optimization of double perovskite-based materials presenting different opportunities for optical applications.

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A PROJECT IN THE FRAMEWORK "NEXTGENERATIONEU": SUSTAINABLE PHOTOELECTROCHEMICAL HYDROGEN EVOLUTION - SERGIO

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The exploration of solar energy for the photoelectrochemical splitting of water into hydrogen and oxygen has been extensively researched as a means of generating sustainable H_2 fuel. However, despite these efforts, commercialization of this technology has not yet materialized. Presently, the primary impediments to commercialization include low solar to hydrogen efficiency (2 3% in PEC with an active area of up to 10 15 cm^2), the utilization of costly and critical raw materials (e.g., $BiVO_4$), and energy losses during the separation of H_2 from O_2 and H_2O vapors in the output stream.
The SERGIO partners have identified an innovative approach to fabricate photoelectrode materials, coupled with a novel scientific direction to achieve cost effective solar driven H_2 production in a tandem photoelectrochemical cell. This project is designed to reach Technology Readiness Level (TRL) 4 by validating the technology in the laboratory using a cell with an active area of up to 10 cm^2, boasting a solar to hydrogen efficiency of 5%, and ensuring acceptable hydrogen purity (99.99%). Our objectives include breakthroughs in cost efficiency, conversion efficiency, and H_2 purity.

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OPTIMITAZION OF ELECTROSPUN NICKEL/MICROPOROUS MATERIAL CATALYSTS FOR METHANATION REACTION

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Nanotechnologies have enabled the creation of compact, high-specific surface area, high-performance devices with many applications in many fields in recent decades. Electrospinning, which produces fibrous nanostructures, is the most promising materials manufacturing method. Its simplicity, low cost, and industrial-scale portability are its key benefits. Safe reproducibility, adaptability, and perfect fibre size control are among its strengths. On the other hand, catalysts are essential in many processes, including decarbonation technologies, which address global warming. In the present research activity, the catalytic systems based on nickel catalysts supported on silica-based micromaterials for simultaneous methanation of oxides carbon has been developed.

The synthesized microporous silica-based materials were MFI (gel precursor obtained using: tetra propyl ammonium hydroxide, water, ethanol, silica source). The loading of metals on the support was made by impregnation on the nanofiber/support obtained by electrospinning. Phase identification, morphology, crystals' dimension, structure properties and thermal stability of fresh catalyst were inspected by XRD, SEM-EDX, HR-TEM, N2 Adsorption/Desorption, Fourier Transform Infrared Spectroscopy (FTIR) and TG-DSC techniques.

Ni/MFI powder, characterized by rounded particle morphology, was used as a term of comparison to evaluate the catalytic performances, in the same experimental conditions. The conversion of CO_2, as well as the production of CH_4 over time were constant for all samples, without any type of alteration during a steam of 15 h. The catalytic activity of electrospun sample Ni/f-MFI compared in terms of CH_4 production and CO_2 conversion, highlight how the catalytic performances were influenced by the nanofibers structure. The CO_2 conversion, as well as CH_4 production, over catalysts supported on nanofibers exhibited an enhancement with respect to the powder reference sample. The scanning electron micrographs of spent catalysts indicated that the fibre morphology of samples was still retained in a compact yet brittle mat. This was the case despite the fact that the catalysts had experienced a partial loss in elasticity and flexibility as a result of continuous activity at high temperatures. These discoveries are particularly intriguing for preventing catalyst leakage, and they are even more so when it is essential to recover the catalyst in a straightforward manner, such as in plug-flow reactors, where there is still a problem in the improvement of the operational stability of samples.

PULSED A SERIES OF CONDUCTING TETRATHIAFULVALENE-BASED 2D MOFs WITH LANTHANIDES IONS (Dy^{III}, Er^{III} & Yb^{III})

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Recently, particular attention has been given to MOFs that exhibit high electrical conductivity with potential applications in electrocatalysis, energy storage, electrochemical sensing, and molecular electronics and spintronics. Among them, tetrathiafulvalene (TTF) linkers have shown promising results due to their redox-active nature and the possibility of generating stable open-shell species, while maintaining their framework.

Materials have been characterized through a Multi-Technique Approach involving: SCXRD, PXRD, Raman Spectroscopy, Quantum Mechanical Calculations, Conductivity Measurements, and AC/DC Magnetic Susceptibility Measurements.

2D Ln-TTF MOFs, formulated as $[Ln_6(TTFTC)_5(H2O)_{22}]\cdot x(H_2O)$(Ln=Dy^{III}, Er^{III}, Yb^{III} and TTFTC= tetrathiafulvalene tetracarboxylate), by layering a methanol solution of the corresponding Ln^{III} salts and an aqueous solution of the TTFTC linker. The structural data revealed a rare 2D topology with 1D open channels (~5Å diameter) filled by water molecules and stacked linker molecules running along [111] direction linked by Dy$_6$ clusters. The different oxidation states of the linker (0, +0.5, +1) were confirmed by structural analysis, micro-Raman spectroscopy and band structure calculation. Conductivity of MOFs as a function of temperature and pressure was measured along single crystal [111] direction, showing a semiconductor behaviour with room temperature conductivity of 1 mS/cm^{-1}, 10 mS/cm^{-1}, and 0.3 mS/cm^{-1} for Dy^{III}, Er^{III} and Yb^{III} MOFs, respectively. AC magnetic susceptibility measurements revealed field-induced slow relaxation of the magnetization for DyIII MOF accounting for two independent relaxation processes with energy barrier U_{eff}=9.5(3) K and U_{eff}= 1.7(5) K.

The MOFs revealed mixed-valence linkers and rare 2D topology. The different oxidation state and strong π-π interaction among linkers allow the formation of good conduction pathway along the [111] direction. The room temperature conductivity values obtained are the highest among TTF-MOFs reported in literature up to now. Furthermore, the Dy-MOF show Single-molecule magnet behaviour under small DC field thanks to the strong magnetic anisotropy.

SPACE-CONFINED 2D AND QUASI-2D HALIDE PEROVSKITE SINGLE CRYSTALS

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Halide perovskites constitute a class of semiconductors renowned for their versatile optical and transport properties. These properties can be fine-tuned through elemental substitutions or crystal structure distortions, making them invaluable in various technological applications such as solar cells, light-emitting diodes (LEDs), lasers, and detectors. While 3D perovskites boast high efficiency, their 2D counterparts offer superior stability and chemical adaptability. Comprising thin layers of perovskite separated by organic cations, 2D perovskites, particularly in their single-crystal atomic configuration, exhibit a multitude of advantageous properties and characteristics.

In 2D single crystals, the absence of grain boundaries enhances electronic properties such as charge transport. Achieving the optimal crystal thickness is crucial for device performance as it prevents carrier loss and ensures effective light absorption, thereby unlocking the full potential of carrier transport. This can be achieved through a space-confined method, which allows for precise control of thickness during perovskite preparation. This aspect is particularly critical for 2D and quasi-2D perovskites, as aligning their crystallographic orientation with the carrier collection direction in solar cells is essential for facilitating conduction. However, 2D perovskites often face challenges with preferential orientation growth, typically parallel to the substrate they are in contact with, thereby insulating carriers within the layers and causing transport issues within the device. To mitigate this problem, the objective is to modify orientation growth using different additives.

This contribution will elucidate my work concerning space-confined and orientation-growth techniques, delving into the processes' intricacies and the resulting outcomes. Specifically, through the confinement of growth within predefined spaces and the introduction of surface modifications, we were able to control the size and shape of the resulting single crystal. Additionally, to alter crystallographic orientation, we introduced additives and utilized functionalized cations as spacers to promote vertical layer alignment. The samples obtained underwent thorough analysis using various techniques, including AFM, confocal microscope, and XRD, to investigate parameters such as thickness, morphology, and orientation.

Implementing space confinement during perovskite preparation emerges as pivotal, playing a crucial role in precisely controlling crystal thickness. This not only enhances device performance but also effectively mitigates carrier loss. Simultaneously, addressing preferential orientation growth, typically parallel to the substrate, becomes imperative. The discussion underscores the importance of space-confined methods, emphasizing their profound impact on advancing the performance of these materials.

PRELIMINARY CHARACTERIZATION OF SPENT ALUMINIUM POWDERS AND THEIR REACTION PRODUCTS FOR HYDROGEN PRODUCTION

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The chemical reaction between aluminium and water is an area of interest in the field of material science due to its potential applications in hydrogen production. In this context, the valorization of spent aluminium powder could be a viable approach to produce hydrogen with a reduced environmental impact. In this study, an experimental campaign was conducted to investigate the reaction mechanisms of two different aluminium powders from waste, containing different proportions of calcium and magnesium as pollutants, during two different heating procedures in an uncontrolled atmosphere (air).

Two powders have been considered in this study, as the outcome of the aluminium casting process, and both underwent to two different heating cycles until 1200°C. After conducting the experiments, samples were subjected to scanning electron microscopy, to determine their morphology, coupled with energy dispersive spectroscopy to evaluate their semi-quantitative chemical composition. Furthermore, a Rietveld refinement was conducted on the X-ray diffraction spectra to estimate the reaction products formulation in terms of crystalline compounds.

Scanning electron microscopy analysis showed that increasing the amount of calcium and magnesium in the aluminium powder (up to 4 wt% as $CaMgC_2O_6$) lead to a highly porous morphology of the specimens after the heating treatment. Furthermore, the Rietveld refinement on the X- ray diffraction spectra indicated that the reaction between aluminium powders and air led to the formation of different aluminium compounds (AlN, A_2O_3, Al_2MgO_4, etc.), also depending on the heating treatment, that could affect further reaction of the spent powders with water for hydrogen production. The most important result was the total absence of pure aluminium after the heating treatment, indicating a strong reactive behavior of the investigated waste powders, and the formation of aluminium compounds other than Alumina, therefore more suitable to enhance the efficiency of the spent powder reaction with water for hydrogen production.

The outcomes of the experiments unequivocally revealed the intricate chemical transformations that aluminium powders engaged with air, resulting in the formation of distinct aluminium compounds such as AlN, Al_2O_3, Al_2MgO_4, among others. Overall, this study provides valuable insights into the reaction mechanism of spent aluminium powders, contributing to exploiting waste to produce hydrogen.

TRANSPARENT NOVEL INSIGHTS ON THE Pd SPECIATION IN Pd/SSZ-13 AND ON THE ROLE OF H_2O IN THE Pd REDUCTION BY CO

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Pd/zeolites are widely employed as heterogeneous catalysts and adsorbers. Recently, the interest towards these materials increased due to their potential application as passive NO_x adsorbers to mitigate in vehicles the problem of cold-start NO_x emissions. Attention was paid to the effects that components present in the exhausts might have on the NO_x storage of these materials, in particular H_2O and CO. Starting from the observation that the reducing effect of CO on Pd is effective only in the presence of water, the present work is focused on the spectroscopic characterization of modifications induced by water and CO at RT on the Pd sites of two different Pd/SSZ-13 samples prepared by impregnation and ion exchange.

The Pd-doped SSZ-13 was prepared by impregnation (1 wt.% Pd) and ion exchange method (0.2 wt.% Pd). The spectroscopic characterization was performed by CO adsorption at room and liquid nitrogen temperature followed by FT-IR spectroscopy on anhydrous and hydrated samples.

Both impregnated and ion-exchanged samples show isolated Pd cations at the exchange sites of the zeolite and PdO_x particles on the external surface. Precise evidences were obtained on how water is necessary in the Pd reduction by CO not only for compensating with H^+ the zeolite exchange sites set available after Pd reduction, but also for mobilizing isolated Pd^{2+}/Pd^+ cations and making possible the reduction reactions. We showed that carbonyl bands in the spectral region 2220-2180 cm^{-1} are mainly related to isolated Pd^{2+} cations on the exchange sites of the zeolite. By the combined effect of CO and adsorbed water at RT, these sites are reduced to isolated Pd^+ sites, whose carbonyl bands fall in the spectral region 2150-2100 cm^{-1}. The aggregation of some Pd^+ sites, just formed by the reduction and mobilized by the hydration, gives rise to the formation of Pd_2O domains. Also, Pd^0(100) sites are observed with CO on hydrated sample and Pd^0(111) sites are formed on the surface of PdO_x particles during CO outgassing. The impregnated and ion-exchanged samples gave the same spectroscopic results in terms of band positions and behaviors, being the band intensities modulated by the different Pd content.

TWO-DIMENSIONAL $CrCl_3$ LAYERED TRIHALIDE SENSOR FOR DETECTION OF HUMIDITY, H_2 AND NO_2

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Hydrogen is considered as the most promising fuel for the transition to a low carbon economy. Though, in view of its wide flammability range (4–75 %), low ignition energy (0.017 mJ) and high combustion heat (142 kJ/g H_2), the risk of industrial outbreak must be lowered by real-time monitoring of its concentration, to detect possible H_2 leakages. However, ambient humidity could influence sensor's response, therefore a simultaneous monitoring of relative humidity is essential to obtain accurate hydrogen measurements. Recently, two-dimensional materials have been demonstrated to be suitable alternatives to traditional metal-oxides (MOXs), to be used as humidity and gas sensors, because of their high surface-to-volume ratios and large extensions of reacting edges. Among the various van der Waals semiconductors, transition metal trihalides (TMTHs, MX_3, where M= transition metal and X = Cl, Br, or I) have attracted scientific attention because of their layered nature and potential in surface-related applications. In this work, we demonstrated that liquid-phase exfoliated $CrCl_3$ exhibits promising capabilities as chemoresistive sensors for humidity, H_2 and NO_2 gases, representing a suitable 2D interface for gas-sensing applications.

$CrCl_3$ was exfoliated via Liquid-phase exfoliation by dispersing commercial $CrCl_3$ powder in Polarclean green solvent. The dispersion containing 2D-exfoliated $CrCl_3$ flakes was spin-coated on patterned Si_3N_4 substrates with Pt interdigitated electrodes and electrical responses characterized.

2D-$CrCl_3$ sensor was used to detect Relative Humidity (RH, 10–80%), H_2 (5–250 ppm) and NO_2 (600 ppb to 1 ppm), in dry/wet air environments at operating temperatures (OTs) of 25°C and 100°C with excellent reproducibility and long-term stability of the electrical response.

Results show that 2D-$CrCl_3$ exhibits p-type responses to Relative Humidity, H_2 and NO_2, increasing/decreasing electrical resistance in reducing/oxidizing environment. The humidity crosssensitivity of 2D-$CrCl_3$ to H_2, reveals that an environment with 40% RH slightly influences the amplitude of H_2 response with no effects on the limit of detection (LOD), which remains constant at 50 ppm. remarkably, humidity is found to boost NO_2 response both in terms of relative response and LOD (improved from 800 to 600 ppb in 40% RH). Disclosing for the first time the humidity and gas sensing response of 2D-$CrCl_3$ interfaces, these findings provide insights and possibilities for using 2D TMTHs as sensitive materials for environmental monitoring.

MESOSTRUCTURED SILICA-BASED MATERIALS AS SORBENTS AND CATALYSTS FOR POLLUTANT REMOVAL AND CCU TECHNOLOGIES

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In recent years, pollution from heavy metals and global warming due to the increasing levels of CO_2 concentration have become global environmental concerns. In this work, mesostructured silicas (MCM-41, MCM-48) were synthesized and functionalized with aminosilanes for the development of amine-silica sorbents with potential applications in Cd^{2+} removal from aqueous solutions and in Carbon Capture and Utilization (CCU) technologies. Thanks to their highly ordered mesoporous structure, the donation of lone pairs by amines to Cd^{2+} and the amines' high affinity for CO_2, amine-silica sorbents are suitable for such applications. Moreover, mesostructured silica-based composites have been developed, through impregnation of MCM-41 with oxidic phases of copper, zinc, and zirconium (CZZ), for a prospective application in the catalytic hydrogenation of CO_2 to methanol.

Mesostructured silica was synthesized with sol-gel method in the presence of a templating agent, a siliceous alkoxide precursor and two different solvent systems: water (MCM-41) and water/ethanol (MCM-48). Various amine-silica sorbents were obtained from post-synthesis grafting with aminopropyltriethoxysilane and tested for Cd^{2+} removal and CO_2 capture. To lower the environmental and economic impact of grafting procedure, an eco-friendly solvent (i.e. butanol instead of toluene) was used. The CZZ@MCM-41 composites were prepared through auto-combustion. Moreover, for the development of cadmium sorbents and CZZ-based catalysts, mesostructured silica from an industrial waste (hexafluorosilicic acid, FSA) was also tested. All sorbents were characterized by XRD, TEM-EDX, TEM, N2-physisorption, thermogravimetric-analysis and ATR-FTIR.

MCM-48 was obtained by adding ethanol as co-solvent, keeping all the other experimental conditions equal to the MCM-41's synthesis, confirming its key role among others synthesis parameters in tuning the mesophase. The replacement of the alkoxide precursor with FSA allowed the production of MCM-41 with analogous textural properties, reducing environmental and economic impacts for CZZ-catalysts' support. The same amino groups' concentration (~2 mmol/g) was obtained for MCM-41 functionalized with toluene and butanol. Amino-silica sorbents were tested for Cd^{2+} sorption showing a removal percentage of 99% and adsorbed amount of cadmium q_e=46mg$_{Cd(II)}$/g$_{sorb}$ at pH 5. This preliminary study suggest that amine-silica sorbents have the potential to remove significant amounts of cadmium ions from aqueous solutions. The use of butanol instead of toluene in the grafting procedure caused a decline in CO_2 adsorption performances (968 μmol$_{CO_2ads}$/g$_{sorb}$ vs. 480 μmol$_{CO_2ads}$/g$_{sorb}$), indicating the need to improve functionalization process. Nevertheless, a comparison revealed that toluene-functionalized MCM-41 is more efficient than SBA-15, emphasizing the crucial role of the support's surface area.

SYSTEMATIC INVESTIGATION ON THE SURFACTANT-ASSISTED LIQUID PHASE EXFOLIATION OF MoS_2 AND WS_2 IN WATER FOR SUSTAINABLE 2D MATERIAL INK

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MoS_2 and WS_2 have gathered significant attention due to their interesting and tunable properties and their wide range of applications. Liquid phase exfoliation (LPE) is a common and facile method to prepare 2D MoS_2 and WS_2. Currently, the principally employed solvents for LPE are expensive, toxic and have high boiling points. Water would be the best option, but surfactants are necessary for LPE in water, since MoS_2 and WS_2 are hydrophobic. Sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS) and sodium hexyl sulfonate (SHS) are selected as surfactants. In this work, we present a systematic investigation on the impact of these surfactants and the variation of their concentration on the LPE of MoS_2 and WS_2.

MoS_2, WS_2, SDS, SDBS and SHS are used without further purification. All the exfoliations are performed using a tip sonicator for 4 hours. In all the experiments, the suspension volume is kept fixed, while the surfactant concentration. After the sonication step, liquid cascade centrifugation is applied at two different rates.

By characterizing and qualifying the products from average number of layers, we find that all the surfactants work efficiently to exfoliate MoS_2 and WS_2 into few layers, and SHS stabilizes the 2D layers better than the other two surfactants.

After the LPE process, it is necessary to confirm the outcome of exfoliation using different characterization techniques such as UV/Visible and Raman spectroscopies, which provides informations on the structural integrity and size of the nanosheets. Regarding the stability of the ink, zeta potential is employed. UV-Visible spectra are also used to gain information on the yield of the product. Thin films of MoS_2 and WS_2 are obtained with Ultrasonic Spray Coater for possible energy-related applications.

STUDY OF THE INFLUENCE OF MEMBRANE SURFACE PROPERTIES ON BUBBLE FORMATION AND RELEASE DURING THE AERATION PROCESS

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Due to their high porosity, porous membranes are a great alternative to traditional systems for promoting efficient oxygen mass transfer from the air to the aqueous liquid phase. The interface, in bubble aeration, is determined by combining the surfaces of the bubbles that rise in the system with the interface contact surface offered by the membrane. To increase the contact area the bubble size is a key parameter, and it is largely influenced by the adhesion to the surface. The strength of the adhesion is linked to the surface characteristics of the substance. This work investigates the effect of the membrane surface properties on the bubble release.
Membranes with different characteristics (material, pore size, configuration, geometry) were used to study the effect of the membrane surface properties on the bubble release. Images of the bubbles formed and released by the membrane surface were captured and analyzed to obtain the number, detachment time, and size of the bubbles. The effect of these parameters on the mass transfer coefficient was evaluated by performing an aeration test with the sodium sulfite method.
Hydrophilic membranes (PVC) produced bubbles with a diameter of 0.5 mm and a high air pressure to generate the bubbles due to water flooding of the pores. Hydrophobic membranes made in PP and PTFE showed the highest bubble dimension (4 and 9 mm respectively) and a tendency to coalesce on the membrane surface but no tendency to pore wetting. PVDF membranes showed the lowest bubble size (0.8 mm), caused by a synergic effect of the contact angle of the material and surface porosity, no coalescence phenomenon on the surface, and the absence of flooding during the operation thanks to their great hydrophobicity. By tuning the surface porosity and therefore roughness it is possible to improve further the number, the size, and the detachment time with a consequent enhancement of the KLa from 0.01 to 0.07 min^{-1}.
In this part of the research, the important role of the proper selection of the membrane (material and features) for the design of a bubble membrane aeration unit was highlighted.
Hydrophilic materials can promote the formation of smaller bubbles than hydrophobic materials. However, the flooding of the pores makes it impossible to use hydrophilic membranes for ventilation. To improve the bubble size in hydrophobic materials is possible to tune the surface porosity and the roughness.

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DISPERSION OF EXPANDED GRAPHITE (EG) IN STEARIC AND PALMITIC ACID MIXTURE FOR THERMAL MANAGEMENT OF PHOTOVOLTAIC CELLS

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In this work phase change materials (PCMs) based passive cooling systems for the revamping of existent silicon photovoltaic (PV) cells were developed and analysed in order to mitigate the efficiency loss caused by temperature rise in the hot season.
A fatty acid mixture having melting temperature closed to 53 °C was exploiting to realize thermal management systems. The PCM was shape stabilized in expanded graphite (EG) at different concentrations (10, 12 and 14 phr) under vacuum into a rotary evaporation apparatus, with the aim to reduce PCM leakage and improve thermal conductivity.
The materials were thermally characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to determine transition temperatures and enthalpies, while the thermal conductivity was evaluated through hot disk tests and laser flash analysis (LFA). The mechanical properties were determined with compression test below and above the PCM melting point. Thermal cycles into climatic chamber were performed to simulate the material response during the three hottest and coldest days of summer 2022 of two Italian locations, Verona and Gela.
The thermal conductivity is improved from 10 to 20 times thanks to the role of EG, also beneficial for leaking reduction, even if to totally avoid it a PE-film encapsulation is necessary. The mechanical properties are detrimentally affected by the temperature due to the large PCM fractions of the samples, even if the plates are able to support small pressures necessary to guarantee the contact with the cell. The thermal management behaviour of the produced plates was verified with the test in climatic chamber, showing delays in reaching 60°C and in some cases complete smooth of the daily peak temperature reached by the PV cell.
The role of expanded graphite is strategic for the processing and the properties of the resulting composites, in order to realize a proper compromise between the thermal enthalpy of PCM and the thermal conductivity of EG, obtaining systems suitable for the heat subtraction from PV cells.

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RAPID FABRICATION OF FE AND PD THIN FILMS AS SERS-ACTIVE SUBSTRATES VIA DYNAMIC HYDROGEN BUBBLE TEMPLATE METHOD

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Portable Raman spectrometers and commercial substrates have made Surface Enhanced Raman Spectroscopy (SERS) a popular analytical technique. Nanostructured materials substrates with high surface area and controlled morphology result in 'hotspots', places of giant electric fields enhancement, where the Raman signals are amplified to high levels, increasing the detection limit. Thin films samples of Fe and Pd, with dendritic morphology, were rapidly fabricated by the Dynamic Hydrogen Bubble Template method, via potentiostatic electrodeposition on a copper substrate. Samples were tested as SERS substrates for the detection of Rhodamine 6G (R6G) dye and they demonstrated good performances, with Pd samples exhibiting the best results.

A three-electrode cell connected to the Autolab potentiostat was used for samples preparation. Platinum grid served as the counter electrode, a double-bridge Ag/AgCl electrode as the reference, and the conductive copper substrate as the working electrode. Electrodeposition was carried out at -4 V and room temperature for 90, 180, and 300 s. The electrolyte used to deposit iron consisted of 0.1 M ferric sulfate heptahydrate as the source of iron and 1.5 M ammonium chloride as a proton source. To deposit palladium, the electrolyte was composed of 0.1 M tetraamminepalladium chloride and 1.5 M ammonium chloride. Samples were characterized using SEM, EDS, and XRD techniques. SERS measurements were conducted using a Renishaw inVia Raman Microscope with a 514 nm laser line, 20 s acquisition time, a 20 ULWD objective, and 0.095 mW laser power at the sample, in rotating mode. The sample was then immersed in R6G dye solutions of varying concentrations for 15 min. Air-drying preceded the measurement of the sample surface.

The microstructure evolves from a dendritic type to nanoparticles in the case of Fe, while for Pd samples, a more classic dendritic shape appears. All the samples are SERS-active and able to enhance the Raman signals for R6G. Pd180s stands out in terms of its performance, with a low detection limit of 10-6 M.

In summary, prepared samples are cost-effective, easy to prepare with a rapid fabrication method, and exhibit noteworthy SERS performance. The superior performance of Pd180s sample can be attributed to its nanostructured morphology, which is extremely conducive to the phenomenon of localized surface plasmon resonance. The precursor salt concentrations required for film formation are relatively low, offering a significant advantage in terms of economic and environmental sustainability of the overall production process.

PHOTO- AND WATER-DEGRADATION PHENOMENA OF ZNO BIO-BLEND BASED ON POLY(LACTIC ACID) AND POLYAMIDE 11

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The purpose of this work is to examine the morphological and chemical-physical changes that occur when ZnO nanoparticles are added to bio-based polymeric materials based on polyamide 11 (PA11) and polylactic acid (PLA). The photo- and water-degradation phenomena of these nanocomposite materials were monitored. For this purpose, the formulation and characterization of novel bio-nanocomposite blends based on PLA and PA11 at a ratio of 70/30 wt.% filled with zinc oxide (ZnO) nanostructures at different percentages were performed.

The effect of nanoparticles (≤2 wt.%) within the blends was thoroughly explored by employing thermogravimetry (TGA), size exclusion chromatography (SEC), matrix-assisted laser desorption ionization–time-of-flight mass spectrometry (MALDI-TOF MS) and scanning and transmission electron microscopy (SEM and TEM).

Adding up to 1% wt. of ZnO resulted in a higher thermal stability of the PA11/PLA blends, with a decrement lower than 8% in terms of molar masses (MMs) values being obtained during blend processing at 200°C. ZnO promoted trans-ester-amide reactions between the two polymers, leading to the formation of PLA/PA11 copolymers.

These species could work as compatibilisers at the polymer interface, improving thermal and mechanical properties. However, the addition of higher quantities of ZnO affected such properties, influencing the photo-oxidative behaviour and thus thwarting the material's application for packaging use. The PLA and blend formulations were subjected to natural aging in seawater for two weeks under natural light exposure. The 0.5% wt. ZnO sample induced polymer degradation with a decrease of 34% in the MMs compared to the neat samples.

STRUCTURE AND MORPHOLOGY OF E-WASTE-DERIVED HIGH VALUE METAL NANOPARTICLES

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The rapid advance of technologies, the increasing demand for electronic devices, and the short lifespans of appliances, have led to a depletion of primary resources and an expanding rate of electronic waste (e-waste). Waste electrical and electronic equipment (WEEE) such as TVs, DVD/CD players, computers, and mobile phones, contains a common valuable component: Printed Circuit Boards (PCBs). Discarded PCBs typically consist of 40% metals, and in particular they represent a valuable resource of precious metals, mainly copper, gold (150-300 ppm) and silver (600-1000 ppm), among many others.

This study focuses on the characterization of metal (Cu, Au and Ag) and metal oxide nanoparticles (NPs) which can be obtained from metals recovered from e-waste such as PCBs. This work was carried out in the framework of the SMART PCBs project (MASE, bando RAEE 2021).

Solutions of recovered noble metals obtained by treating the shredded PBCs with appropriate selective and eco-friendly leaching mixtures were used as precursors for the production of NPs. Then, either thermal decomposition or several chemical reduction approaches were conducted to obtain NPs by using various types of reducing and/or capping agents. Ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), and X-ray powder diffractometry (XRD) were used to characterize morphology and crystallinity of NPs.

The color solution appeared to gradually change as NP formation occurred. UV-vis spectrophotometry confirmed the occurrence of metallic nanoparticles, supporting the occurrence of ion reduction and nanoparticle formation. Likewise, both XRD and TEM corroborated the crystalline nature, phase purity, shape and size of the manufactured NPs.

The investigation of the products obtained by both thermal decomposition and several chemical reduction approaches suggests that NPs characterized by peculiar sizes, shapes and crystal structures can be generated from recovered metal ion solutions.

NEW AND SEMPLIFIED FABRICATION METHOD OF Li_4SiO_4-K_2CO_3-BASED PELLETS FOR CO_2 CAPTURE AT HIGH TEMPERATURE

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Post-combustion treatments of hot flue gases from power plants based on amine-scrubbing systems represent the only methods that have reached the required technology readiness level for widespread commercial adoption. Unfortunately, this technique carries a significant energy penalty, attributed to its high energy demands for the absorption solution regeneration and maintenance costs. To address this challenge, extensive research efforts are currently underway to explore new solutions based on solid sorbents for reducing CO_2 emissions. Within this context, the present study introduces a simplified pelletising technique designed to produce innovative, solid, and durable pellets with enhanced CO_2 capture capacity and cyclability. These advancements render their application feasible in industrial fixed-bed adsorption systems.
Li_4SiO_4 powders were synthesised from quartz silica (SiO_2) and lithium carbonate (Li_2CO_3), followed by the addition of different amounts of K_2CO_3 (10-30 wt.%) as an activity promoter and viscous linear polyalphaolefins as a binder and pore-forming agent. The resulting mixture was extruded into cylindrical pellets and sintered at moderate temperatures (550 °C) to produce porous and mechanically resistant sorbents. The sorption/desorption performance of the resulting pellets was assessed by thermogravimetric analysis at high temperatures. XRD, BET, and SEM analyses were conducted to determine the composition, and the textural and morphological properties of the developed sorbents, respectively.
The results indicate that an optimal K_2CO_3 content of 20 wt.% facilitates the formation of a homogeneous molten K_2CO_3-Li_2CO_3 mixture during CO_2 chemisorption, thereby preventing phase segregation across multiple cycles. The inclusion of 30 wt.% olefin yields durable, porous pellets capable of maintaining a consistent and regenerable CO_2 sorption capacity of 130 mg $CO_{2/g}$ (corresponding to a Li_4SiO_4 conversion of 45%). The designed cylindrical pellets (15 mm x 20 mm) exhibited a BET surface area of about 1.5 m^2/g, similar to that of the starting K_2CO_3/Li_4SiO_4 powder. The stability of the pellet was successfully tested over 25 repeated sorption/desorption cycles (30 min each).
The existing body of literature concerning Li4SiO4-based pellets has predominantly focused on complex chemo-mechanical fabrication procedures. These methods typically entail the incorporation of solvents and binders to ensure the homogeneous dispersion of materials and pore-formers. In this context, the present research presents a novel and single-step pelletizing technique designed to facilitate the production of robust and porous pellets with enhanced CO_2 capture capacity and cyclic stability.

OPTIMIZATION OF BIOFUEL PRODUCTION BY MICROBIAL FERMENTATION: A NEW STRATEGY FOR MONITORING SUBSTRATES CONSUMPTION AND METABOLITES RELEASE

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The growing concern for global warming and environmental risks need the development of new methods to produce alternative and renewable energy sources, such as biofuels, to reduce the carbon footprint. Among different mechanisms of biofuel production, bacterial-mediated fermentation processes get great interest in the scientific community due to their eco-friendly features and low production costs.

Biofuels like bioethanol, biomethane and biohydrogen can be produced by dark- and photo-fermentation of organic substrates, which involve numerous and complex metabolic pathways. In this context we propose a fast analytical approach, based on attenuated total reflectance Fourier transform infrared (ATR-FTIR) difference spectroscopy, to assess substrates intake and metabolites release by growing bacteria.

Enterobacter aerogenes and *Rhodobacter sphaeroides* were grown in appropriate culture media in anaerobic conditions. Then ATR-FTIR spectra of their culture media were recorded. The spectrum of the initial culture medium, immediately after bacteria inoculum, was used as reference background for collecting ATR-FTIR difference spectra of liquid media as arising from microbial growth modification. Standard compounds spectra were employed for guiding band assignment and identifying characteristic components producing either negative (consumed substrates) or positive (released metabolites) signals in difference spectra.

Biohydrogen production by microbial fermentation was demonstrated for both bacterial strains. In the case of Enterobacter aerogenes metabolism, the analysis of difference ATR-FTIR signals revealed that only glucose is degraded, while ethanol and 2,3-butanediol are the main soluble metabolites released. In the case of photo-fermentation by *Rhodobacter sphaeroides* the partial consumption of organic acids and the complete utilization of glutamic acid were proved.

In the present study, the potential of the ATR-FTIR difference spectroscopy in the field of microbial biochemistry and biotechnology for applications in ecological transition and sustainable mobility was highlighted. This fast and reliable analytical approach could represent a powerful strategy to screen different bacterial strains and to select suitable raw and waste materials to be employed in the field of biofuel production.

FLASH SINTERING OF CARBIDES AND BORIDES

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Flash sintering was officially discovered about fifteen years ago as a ground-breaking method to consolidate ceramics in very short time at temperature much lower than that used for conventional sintering. Since then, it has been applied to several ceramics and composites with the common feature to be characterized by a negative temperature coefficient (NTC) for resistivity while few attempts have been made on materials with metal-like electronic conduction like hard ceramics, i.e. borides and carbides.

WC and ZrB_2 commercial powders were used in the present work. Flash sintering experiments were carried out using a custom-made apparatus operating in lab air, which allowed to control the applied pressure and voltage, temperature and displacement. The obtained materials were characterized from a physical, structural and mechanical point of view.

Both tungsten carbide and zirconium diboride can be successfully flash sintered by using optimized processing conditions in very short time (less than a minute). Final microstructure, density and mechanical properties (like hardness and fracture toughness) depend on three fundamental processing parameters like surface chemistry of the starting powder, applied pressure and voltage.

Sintering behaviour is correlated with a thermal runaway phenomenon generated by the extrinsic NTC behaviour of the powder compact at the beginning of the process although the considered materials are intrinsically PTC (positive temperature coefficient for resistivity) like metals. Surface chemistry of the starting powder and pressure have a fundamental role in the densification behaviour since they determine the initial electrical resistance of the powder compact and, therefore, influence the power which is initially dissipated in the material to activate the diffusional phenomena necessary for sintering.

The results of the present work greatly expand the potentiality of flash sintering as an efficient, low-energy intensity process for metals and, especially, hard ceramics.

HIGHLY STABLE $CsPbBr_3$ PEROVSKITE PHASES FROM NOVEL β-DIKETONATE GLYME ADDUCTS

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Lead ion is one of the key metals of the all-inorganic lead halide perovskites. This work tailors novel architectures of lead's coordination sphere using a β-diketone (H-hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) and a glyme [monoglyme (1,2-dimethoxyethane), triglyme (2,5,8,11-tetraoxadodecane) or tetraglyme (2,5,8,11,14-pentaoxapentadecane)] ligand. To validate the potentiality of these "$Pb(hfa)_2$•glyme" precursors, a facile, one-step and low-temperature solution approach has been applied to prepare $CsPbBr_3$ microcrystals with a process carried out in air at atmospheric pressure.
Novel lead complexes have been synthesized, in a single step reaction, from the lead oxide, hexafluoroacetylacetone, and glyme ligands in dichloromethane Coordination chemistry of these $Pb(hfa)_2$•glyme adducts have been analysed through FT IR spectroscopy, ^1H and ^{13}C NMR analyses. The synthesis of the $CsPbBr_3$ microcrystals took place through a precipitation reaction in an ethanol solution containing Cs(hfa) and "$Pb(hfa)_2$•glyme" by adding liquid Br_2 Morphological, compositional, and crystallographic characterisation were carried out by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Energy Dispersive Xray analysis (EDX). Optical band-gaps have been evaluated through Tauc plots starting from UV-visible absorbance spectra of the dispersions of $CsPbBr_3$ microcrystals.
Single-crystal X-ray diffraction studies provide evidence of the formation of monomeric $Pb(hfa)_2$•monoglyme structure. FT-IR spectroscopy, ^1H and ^{13}C NMR analyses indicate the coordination of the lead ion by hfa and polyethers. For the $CsPbBr_3$ microcrystals, FE-SEM indicates a good uniform morphology of cubic grains, while the structure and the 1:1:3 stoichiometry of Cs:Pb:Br is confirmed by XRD and EDX, respectively. XRD patterns of the six-month aged $CsPbBr_3$ powders do not exhibit relevant changes with respect to the initial patterns suggesting the preservation of the perovskite structure. Tauc plots point to optical energy band-gaps (Eg) in the 2.21–2.27 eV range.
Novel lead complexes of the type "$Pb(hfa)_2$•glyme" were synthesized using a single-step reaction. These adducts have been successfully applied as precursors in a green solution synthesis of pure $CsPbBr_3$ microcrystals. It is worthy of note the excellent stability of the perovskite $CsPbBr_3$ microcrystals even after six months of storage in ambient conditions. The good optical properties for this type of systems enables a variety of applications, such as energy conversion and photocatalysis. The present green solution synthesis shows numerous benefits including the absence of unsafe organic solvents and the mild working environment (room temperature and atmospheric pressure).

ACCELERATED CORROSION ASSESSMENT OF AA1050 EXPOSED TO E27 BIOFUEL

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In recent times, there has been a surge in global attention towards biofuels as a viable alternative to traditional fossil fuels in the realm of transportation. This trend is in line with international initiatives aimed at curbing greenhouse gas emissions and reducing reliance on crude oil. Bioethanol, among the array of biofuels available, emerges as a prominent option due to its widespread availability, straightforward production methodologies, and compatibility with existing infrastructures. Its utilization in automotive fuels can be either as an additive or a complete replacement for gasoline. However, there is a paucity of empirical data concerning the corrosive properties of bioethanol blends, particularly those exceeding 10% (E10), which may trigger unpredictable non-linear corrosive reactions on aluminium alloys, particularly under elevated engine temperatures. This research endeavors to explore the corrosion behaviors and underlying mechanisms of the AA1050 aluminium alloy when exposed to a blend comprising 27% bioethanol (E27) mixed with gasoline.

Experiments were conducted in an autoclave at 100 °C for three days, under oxygen exposure. Samples were then analysed using X-ray diffraction, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) to examine surface oxide formation. Corrosion studies were conducted by means of polarization curves, Open Circuit Voltage measurements and Electrochemical Impedance Spectroscopy (EIS). The corrosion rate was measured accordingly with the experimental conditions.

It has been observed that following a three-day immersion in the biofuel within an autoclave, not under vacuum, at 100°C, the specimens underwent complete deterioration, leading to the formation of corrosion products such as boehmite and bayerite, two aluminium hydroxides. Conversely, for the samples immersed under vacuum conditions with the flow of nitrogen at a temperature of 100° C for the same duration, no macroscopic changes occurred, with no observable corrosive phenomena.

As indicated in the literature and confirmed through laboratory experimentation, temperature, the presence or absence of oxygen during measurements, and the percentage of water in the fuel are critical parameters for comprehensively understanding corrosive phenomena. Indeed, it has been observed that a temperature equal to or exceeding 80 ° C leads to the formation of alcohol molecules that continuously attack the surface of the specimens, ultimately resulting in corrosion. This phenomenon occurs irrespective of the water percentage within the fuel, which significantly influences the formation of protective oxides on the metal surface. In fact, with a minimal water percentage, corrosive phenomena are highly probable, as water tends to serve a protective and passivating role on surfaces.

GREEN UP: GREENER NANOMATERIALS FOR UPCONVERSION IN PHOTOCATALYTIC APPLICATIONS

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In photovoltaic (PV) cells, a large fraction of the solar spectrum is not exploited: besides the losses due to thermalization (33 %) and charge extraction (15%), 23% of the solar radiation in the NIR (Near Infra-Red) and IR range is not absorbed by "conventional" Si solar cells, but also Dye-Sensitized Solar Cells (DSSC) and perovskite solar cells suffer from such NIR losses.

This poster presents the activities of the GREEN UP project funded through the PRIN 2022 call by the Italian Ministry of University and Research. GREEN UP aims at identifying greener nanomaterials for light upconversion than the state-of-the-art and to exploited them for photocatalytic applications.

Through the combined use of TD-DFT calculations and different synthetic techniques, the project is pursuing the target of developing new generation hybrid nanomaterials to allow a more efficient and spread use of solar light for chemical reactions.

"This study was carried out within the « GREEN UP: GREENER NANOMATERIALS FOR UPCONVERSION IN PHOTOCATALYTIC APPLICATIONS» project –funded by the Ministero dell'Università e della Ricerca –within the PRIN 2022 program(D.D.104 -02/02/2022) funded by the European Union - Next Generation EU. This manuscript reflects only the authors' views and opinions and the Ministry cannot be considered responsible for them".

DESIGN, REALIZATION AND CHARACTERIZATION OF BIOCOMPOSITE MATERIALS BASED ON BREWER'S SPENT GRAIN

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The wood plastic composite (WPC) market has been gaining momentum in recent years, and the increasing scarcity of forest biomass, rising wood flour prices, and concerns about the use of traditional polymer matrices are driving research to investigate new biocomposite materials for the circular economy. Brewer's spent grain (BSG) is a particularly interesting agro-food waste for use as a lignocellulosic filler in the creation of WPCs. The work aims to evaluate the BSG filler influence on the composite properties.

Two different biopolymer matrices, namely polybutylene succinate (PBS) and poly-3-hydroxybutyrate-co-3-hydroxyhexanoate (PHBH) were used to produce the biocomposites. Three different types of BSG fillers were added at four different concentrations (10, 20, 30 and 50%). The composites were made by twin-screw extrusion and injection molding. Obtained specimens were used for further rheological and thermo-mechanical characterization.

The melt flow index (MFI) of PBS-based composite samples decreases as the filler content within the polymer matrix increases, unlike PHBH-based composites where an increase in MFI values is evident. Regarding mechanical analysis, all composites respond with an increase in Young's modulus and a decrease in toughness and elongation at break as filler content increases. No change in melting temperature and glass transition is noted in contrast to a decrease in crystallinity.

The decrease in MFI values for PBS-based composites can be attributed to the addition of filler within the polymer matrix, which imposes a limitation on the mobility of the chains. This was also confirmed by the results obtained from the mechanical properties. Unlike the PHBH-based composites, where an increase in MFI values was noted due to the degradation of the polymer matrix, as can be expected for a polyhydroxyalkanoate.

Obtained results show that realized biocomposites can be attractive for large-scale applications, as they present a high added value from the environmental point of view.

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DEVELOPMENT OF CELLULOSE BIO-BASED RECYCLABLE BIOCOMPOSITES FOR 3D-PRINTING AND INJECTION MOLDING ITEMS

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Bioplastics have gained traction as eco-friendly alternatives to conventional polymers, designed to naturally degrade over time. However, biodegradability alone is not sufficient to address the plastic waste problem; indeed, biodegradation provides an option for disposing waste in natural environments, but recycling offers a more efficient and environmentally friendly solution. Integrating recyclability into biodegradable polymers not only reduces environmental impact but also contributes to a more circular and economically sustainable model. In this context the present work aims to develop recyclable cellulose-based biocomposites tailored for injection molding and 3D printing applications.

The materials used are polybutylene succinate (PBS FZ71PM) as matrix and short cellulosic fibers (Arbocel) at 10 and 20 wt.%. To simulate the achievement of recycled pellets, PBS has been twin-screw extruded for five cycles with a semi-industrial twin-screw extruder equipped with two 25 mm co-rotating screws with L/D = 44 before to produce, always in the twin-screw compounder the biocomposites. The extruded pellets were sent to both injection molding (IM) and 3D printing (3DP) machines to produce dog-bone specimens (ISO 527-1A) useful for mechanical characterizations. Also thermal, rheological and morphological analysis have been carried out.

Starting from Melt flow results, they showed a trend of slight increase in MFR after further re-processing cycle. In fact, the high temperature and shear applied to the melted material during processing tend to break the chains of the polymers, degrading the material. In any case also the values achieved for PBS recycled 5 times are suitable for secondary processes like IM and 3DP. The dog bones produced with these two techniques for the reprocessed PBS matrix showed modulus, stress at break and deformation values in the range of the typical fossil-based recycled polyolefins. The Charpy Impact Resistance value decreases with an increasing number of cycles, with a more pronounced drop from first cycle to third cycle compared to the transition from 3rd cycle to the 5th.

By encouraging the development and implementation of advanced recycling technologies, opportunities can be created for a more sustainable economy and a greener future. Combining biodegradability and recyclability in polymers represents a key strategy for addressing current environmental challenges.

This work aims to demonstrate that a recycling process simulation does not significantly compromise the properties of PBS, and the reprocessed PBS can be used as matrix to produce biocomposites with cellulose short fibre for IM and 3DP applications.

HEMP FIBERS MODIFIED WITH GRAPHITE OXIDE AS GREEN SOLUTION FOR WATER REMEDIATION

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Hemp fibers (HF) were modified with graphite oxide (GO) through grafting with (3-Aminopropyl)triethoxysilane (APTES) for the removal of methylene blue (MB) from aqueous solutions. The morphological and spectroscopic analyses confirmed the covering of GO onto HF. Kinetics studies concerning the adsorption of MB were carried out analyzing the effect of pH l, temperature, and MB initial concentration. GO modification contributed to increase the MB adsorption capacity changing from 36.7 mg/g for raw HF to 53.86 mg/g after the modification with an increase of about 32%. Plateau regime was achieved after 30 minutes while the adsorption capacity was found to be directly dependent on contact time. Maximum adsorption capacity slightly increases with temperature indicating that the process is slightly endothermic (ΔH=3.43 KJ/mol). Even the pH plays an important role on adsorption process, indicating that weak electrostatic interactions could exist between cationic dye and electron rich sites of surface. In particular, adsorption capacity increases from 37 mg/g to 44 mg/g from pH=3 to pH=12 (T=20°C), from 46 mg/g to 49 mg/g from pH=3 to pH=12 (T=50°C) and from 45 mg/g to 49 mg/g from pH=3 to pH=12 (T=80°C). This decrease in adsorption capacity changing from pH=7 to pH=12 might be due to the partial decomposition or damage caused by alkaline environment to certain adsorption sites or functional groups. The equilibrium adsorption capacity of the adsorbent for methylene blue increased with increasing initial dye concentration. For example, at pH=7.5 and T=20°C, the adsorbed amount changed from 54 mg/g to 372 mg/g, as the adsorbate changed from 5 to 35 mg/L. The removal of dye appears to be concentration-dependent since the higher initial concentration contributed to increase the driving force which overcomes the resistance to the mass transfer of dye between the aqueous and the solid phase. An increase in salt concentration resulted in a decrease of MB adsorption, ascribed to the competition between the MB cations and salt cations to occupy the adsorption sites. A mathematical algorithm was applied to individuate the optimal set of process parameters (pH=9.25, T=53.8°C and C0=13.2 mg/L) which maximizes the removal capacity. Regeneration studies showed 15% drop in adsorption capacity after 30 cycles. The reported adsorption mechanism contributed to give more insight into the complexity of adsorption phenomena on natural materials, which can be due to electrostatic interactions, H bonding and π–π conjugations.

3D-PRINTABLE LEATHER SCRAP-POLYMER COMPOSITE MATERIALS IN A CIRCULAR ECONOMY PERSPECTIVE

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Leather production is resource intensive, demanding substantial water and energy for tanning, often employing hazardous chemicals like chromium. These processes contribute disposal issues (e.g. for incineration) and harm ecosystems, with a significant carbon footprint from energy intensive stages. Synthetic alternatives are available on the market, but they are typically petrol base d and lack recyclability In this context, additive manufacturing, particularly Direct Ink Writing (DIW), offers a promising way to repurpose leather solid wastes from shavings as fillers in leather polymer composites, providing advantages such as rapid and cost effective material formulation, low energy consumption, and exceptional material versatility Leather wastes has been used as a filler for the formulation of polymer based, 3D Printable composite materials. On this basis, mimicking the properties of original leather is the first step for circular economy in leather industry.

UV and thermally curable resins have been employed as matrices, leading to the development of both rigid and flexible materials. Rheological behaviour has been investigated in order to quantify the printability of the formulations. Proper crosslinking and mechanical properties have been characterized in order to assess the suitability for the scope.

The composition based on a rigid resin has shown poor printability, due to the filler resin compatibilization process. However, the mechanical properties of cast composite sample are similar to the ones of the neat resin. The composition based on a flexible resin has shown good printability and higher mechanical properties with respect to the neat resin.

Leather solid wastes from shaving has been successfully used for the formulation of two 3D Printable leather polymer composites. Using a rigid matrix, the material shows poor printability, but neat resin mechanical properties have been preserved by adding up to 15% leather waste. Therefore, the material is suitable for casting applications. Using a flexible matrix, the material shows a good printability and higher mechanical properties with respect to the neat resin by using up to 51% leather solid wastes from shaving In addition, such material closely resembles virgin leather mechanical properties, paving the way f or a circular economy approach and the production customized items.

This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

THE ROLE OF FLUORINE FUNCTIONALIZATION ON THE FLEXIBLE BEHAVIOUR OF NOVEL Ce/Al-BASED METAL ORGANIC FRAMEWORKS

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The strength of Metal-Organic Frameworks (MOFs) lies in the unlimited possibility of tuning their textural properties. Furthermore, some MOFs, labelled as flexible, are characterized by dynamic features of their framework. The synthesis of fluorinated MOFs is relevant since fluorine atoms can impartexcellent properties, including framework flexibility.

The (per)fluorinated version of commercial MIL-53(Al) and Al-FUM (F_4_MIL53(Al) and Al-TFS, respectively) and a series of F_x_MIL140(Ce) have been synthesized and studied with different techniques. In particular, in situ PXRD with IR and SSNMR spectroscopies have been employed to characterize the phase changes. Through volumetric measurements, different probes have been employed, carefully following the changes in shape of the isotherms as a function of the analysis temperature.

In situ DRIFT and PXRD allowed to disclose the flexible behavior of per-fluorinated Al-MOFs, pointing out the main differences with their respective analogues. Upon water removal, Al-TFS undergoes an expansion of the cell volume revealing a breathing behavior. This has been highlighted by the peculiar shape of the volumetric CO_2 isotherms. F_4-MIL53(Al) is also a flexible MOF, as its protonated analogue, but the presence of fluorine atoms affects such behavior. For example, CO_2 isotherms exhibit a step at high relative pressure (RP) due to the expansion of the pores, but do not display a S-shape at very low RP, as instead occurs with MIL53(Al). Finally, the degree of fluorination on the linker of different F_x_MIL140(Ce) is crucial for a cooperative rotation of the rings upon CO_2 adsorption, together with a stronger acidic character of Ce^{4+}.

The possibility to tune flexibility upon adsorption of CO_2 is a key point. For S-shaped isotherms, it is possible to reduce the energetic cost of adsorbent regeneration and reach an easy release of the CO_2 adsorbed. Moreover, the transition triggered by a specific adsorptive increases its selectivity, enhancing the performances in gas separation processes.

CERIUM DOPED METAL ORGANIC FRAMEWORKS CATALYSTS FOR WATER SPLITTING REACTION

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The search for new forms of energy vectors, avoiding the use of fossil feedstocks, is pushing the research towards greener solutions. Molecular hydrogen from green and sustainable sources is one of the best candidates for this role. Currently, it is mostly produced by cracking and reforming of non-renewable starting materials. Extremely abundant on Earth and pretty evenly distributed, water is probably the most common hydrogen-containing molecule; however, its chemical stability makes it difficult its use as hydrogen source. Nevertheless, through photosynthesis, plants employ water as source of hydrogen since billions of years. The core of this process stands in the Photosystem II, based on a tetranuclear Mn metal cluster. Metal Organic Frameworks (MOFs) are synthetic hybrid materials based on metal clusters connected via organic linkers to form a virtually infinite crystalline ordered structure with extremely high values of specific surface area. Here we present two classes of MOFs, with potential electrocatalytic activity towards water splitting process, in particular the Oxygen Evolution Reaction (OER).

Two different MOFs structures were prepared, namely MOF-808 and MOF-74. The first one has Zr-based clusters and was doped with Ce4+ cations, while the second one has Zn-based clusters and was doped with Ce^{3+} cations. Both materials were characterized with several physico-chemical techniques, such as XRD, N_2 adsorption, TGA, SEM, EDX, ICP-MS, and ATR-MIR. Once their properties were verified, they were deposited onto electrodes and tested with cyclic voltammetry (CV), in order to check their response and their stability under potential reaction conditions.

Doping was attempted with several cerium amounts; however, for MOF-808 the best results were obtained with a Zr:Ce ratio 2:1, while for MOF-74 optimum properties were achieved with a Zn:Ce ratio 9:1. The obtained materials displayed high crystallinity and surface area values, united with an even distribution of Ce inside the structures. Concerning CV measurements, both materials evidenced the oxidation and reduction peaks of cerium species present. Over several cycles, both materials maintained almost unaltered their electrochemical behavior, confirming that the insertion of a more active redox metal (such as cerium) inside a more stable matrix (Zr^{4+} for MOF-808, and Zn^{2+} in the case of MOF-74) is a good strategy to enhance materials stability. The next step that will be shortly attempted, is to test the catalysts for OER.

FIBRE-BASED PACKAGING AND DISPERSION COATINGS: INVESTIGATION ON THE BARRIER, CONVERTING, AND RECYCLING PERFORMANCE

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Recently, the fibre-based food packaging sector experienced renovated material innovation. The industry wills to introduce dispersion coatings (DCs) as alternative technology to extrusion coating (EC) and lamination. DCs allow low non-cellulosic contents since processed as inks. The work aimed to broadly characterize the barrier, converting, and recycling properties of DCs meant for food packaging applications.

Four paper and two paperboard substrates were rod-coated with developed or commercial DCs. The developed coatings featured a low-Tg and highly cross-linked styrene-butadiene latex filled with kaolin or talc ratios (up to 60% w/w). Water, moisture, and grease barrier properties were investigated. Processing properties included fold cracking, creasing, heat-sealing, blocking, and tray-forming ability of 1/9 foodstuff containers. Recyclability was assessed according to recent laboratory methodologies.

The coat grammage ranged from 7–12 g/m^2 for paper and paperboard, respectively. Water and moisture barrier reduced up to 0.1 g/m^2 and ~20 g/m^2, similar to EC substrates; grease permeation time was up to >24 h. Increasing pigment content improved moisture and grease barrier, whereas proved detrimental due to coat defects or hydrophilic nature of the pigment. The low-Tg minimised fold cracking (higher along machine direction and having the coating facing outside the fold), achieving the lowest values compared to commercial DCs. Developed DCs could heat-seal at temperatures as low as 80°C (increasing filler content require higher temperatures, up to no sealing at 140°C for 60% w/w of kaolin), compared to 160°C of EC. The sealing ability was proportional to the blocking tendency. Paperboard trays were produced from dispersion-coated substrates. Higher moisture contents negatively affected the dynamic friction coefficient, leading to increased blocking tendency. The produced trays showed process-induced coat defects due to high blank holding forces and pressing speeds. The materials could be easily recycled; however, the macrostickies were high and negatively impacted on the UNI 11743:2019 testing methodology.

The dispersion coating technology presents remarkable features, characterized by good barrier and processing properties. Pigment content (+) modulates the coating stickiness (−), barrier (+), and cracking resistance (−). Dispersion-coated paperboard trays can be produced but demanding converting processes are critical. Reducing the non-cellulosic content while transitioning from other technologies is currently the major challenge at industrial production yields. Sufficient processing properties, i.e., flexibility and toughness, are mandatory to achieve interesting industrial solutions; much effort should be placed in the tweaking of the latex to withstand a high elastic deformation, still providing sufficient barrier properties.

EFFECT OF ADDING MANDARIN PEELS POWDERS ON BIOPOLYMER BLENDS

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Organic waste from food production represents a valuable resource for biomass and biomaterial production. In this context, various food wastes such as tomato, mango, avocado, and banana peels are being incorporated into biodegradable polymeric matrices to harness their biodegradability advantage.
Biocomposites were prepared using a corotating twin-screw extruder with a screw diameter of 19 mm and an L/D ratio of 35 mm, incorporating 10 and 20 wt. % of MPP into a biodegradable blend known as Bio-Flex®. This commercial blend comprises poly(lactic acid) (PLA) and poly(butylene adipate co-terephthalate) (PBAT). The mandarin peel powders were obtained by grinding the Tardivo di Ciaculli species, an endemic variety in the Palermo area. Prior to grinding, the peels were dried in an oven at 90 °C for 48 hours.
Morphological, mechanical and rheological characterizations were performed on the resulting biocomposites. The results clearly demonstrate that the incorporation of MPP affects the rheological behavior and the mechanical properties of the biocomposites.
Specifically, the flow curves of the biocomposites do not exhibit a Newtonian plateau at low frequencies, instead showing pronounced shear thinning behavior. Additionally, at high frequencies, the viscosity of the biocomposites is lower than that of the matrix. Moreover, as the filler content increases, the curve progressively rises. The mechanical test results reveal that the addition of MPPs leads to an increase in the elastic modulus. However, the tensile strength decreases due to low values of elongation at break. The intrinsic viscosity of PLA, PBAT and their biocomposites was measured and the results confirm that both for PLA than PBAT a decrease in molecular weight is evident. These results highlight the degradative effect of mandarin pells powder added as fillers. Probably this result is due to a catalytic effect by mandarin peel on hydrolytic scission phenomena on PLA and PBAT.

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MECHANISM AND PROPERTIES OF EMERGING LEAD-FREE BCZT PEROVSKITE

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The rising concern for the environment is turning the research on the development of sustainable processing routes to manufacture safe and viable piezoelectric materials that can replace the commercial Lead Zirconate Titanate (PZT). Among the most interesting lead-free alternatives, the pseudo-ternary Barium Calcium Zirconate Titanate (BCZT) is increasingly drawing the attention. Within this context, in-depth knowledge of the system under study is the key for implementing and improving materials processing, to further develop scalable, economical and environmentally friendly production routes. Hence, at the current state of the art, the details concerning the formation mechanism of the BCZT perovskite, which can vary deepening on both precursors and synthetic approaches, should be further clarified.

In this work, the impact of combined ball-milling and freeze-drying techniques on the overall formation kinetics of $(Ba_{0.92}Ca_{0.08})$ $(Ti_{0.9}Zr_{0.10})$ (BCZT) system, was investigated. To compare the different behaviour of the untreated and activated precursors, multiple characterisation techniques, such as combined TGA/DSC (2, 5, 10°C/min), ex situ XRD and in situ high-resolution synchrotron T-ramp P-XRD measurements were used.

The results obtained confirmed the formation of a single perovskite phase with a higher degree of purity at a lower temperature ($\Delta T=200°C$) for the post ball-milled and lyophilized powders.

Discussion

The potential of investigated routes for the fabrication of high-performance lead-free BCZT piezoceramics, the optimal electromechanical properties achieved and some of the related challenges, are also briefly discussed.

SELECTING MOLECULAR OR SURFACE CENTERS IN CARBON DOTS-SILICA HYBRIDS TO TUNE THE OPTICAL EMISSION

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In recent years, significant efforts have been directed towards replacing semiconductor quantum dots and rare-earth-based materials in optoelectronics and photonics with environmentally friendly and cost-effective alternatives. Carbon Dots (CDs) have emerged as a promising candidate due to their efficient and tunable emission properties, facile chemical functionalization, surface passivation, chemical inertness, resistance to photobleaching, and biocompatibility. This study investigates CDs synthesized within solid-state matrices of commercially available mesoporous silica using a static open-air oven synthesis method. The photophysical properties of these solid-state hybrids were compared with those of reference CDs prepared without silica matrices and dispersed in water.

We performed a bottom-up synthesis starting with citric acid and urea, which assembled inside two different silica matrices (commercial MCM-48 and SBA-15), leading to the formation of two carbon dots-silica hybrid systems. Their structural and optical properties were characterized using TEM, ATR, XPS, UV-Vis, steady-state, and time-resolved photoluminescence.

In silica, we observed a variation in the optical properties of the CDs compared to the nanoparticles dispersed in water, with an increase in the green emissive band relative to the blue band. The interaction with the matrix was confirmed by studying the irradiation effect on the hybrids over time, which resulted in an overall increase in the green luminescence intensity in the hybrid. XPS measurements showed a higher degree of doping at the expense of the pure aromatic systems and different types of nitrogen dopants. TEM images, obtained after extracting carbon dots from the host matrix, demonstrated that silica could serve as a suitable nanoreactor to control the size and distribution of these particles.

The synthesis of CDs in a silica environment favored greater control over nanoparticle size and the production of more green-emitting centers, whereas synthesis outside of silica resulted in less size control and a higher production of blue-emitting channels. Furthermore, we investigated the luminescence properties in these two environments, revealing that in silica, emission is primarily attributed to surface centers. Their interaction with the matrix is enhanced by irradiation but hindered by molecular aggregation-induced quenching. Conversely, in water, molecular centers are predominantly observed.

POLYMERIC WASTE PYROLYSIS, KINETIC ASPECTS AND PRODUCTS VALORIZATION

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As polymeric waste recycling consolidates, a huge portion of polymeric wastes is still impossible to be processed by any means. The only diffused alternative to landfill is their use as secondary solid fuel (SSF) for energy generation by combustion. Pyrolysis can be considered as a tertiary recycling way able to produce a wide variety of high value products while reducing CO_2 emissions. Although this technology is well-known its diffusion is still very limited due to the complexity of the processes happening during pyrolysis and to the high variability of the polymeric waste composition and presence of other heterogenous materials (e.g. paper) that leads to results that are difficult to predict and generalize. The main goal of this work was to perform studies on thermal decomposition of a commercial waste polymers mixture mainly made of polyolefins.

The study is mainly centred on a commercial polymeric mixture produced from plastic waste. Kinetic studies were conducted by the application of different model-free approaches (e.g. Kissinger, Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose models) to results of thermogravimetric analysis (TGA) run at different scan rates on the polymeric waste material and for comparison on its pure components identified by infrared spectroscopy. A discontinuous lab scale plant was set up to perform pyrolysis tests under N_2 atmosphere in different thermal conditions to determine the yield and composition of both liquid and gas products. Liquids were collected by fitting the plant with an efficient condensation zone, then they were characterized by infrared spectroscopy, gaschromatography-mass spectrometry and thermal analysis. Gas products were analyzed with an online micro-gaschromatograph.

TGA scans showed a great loss of weight between 400°C and 500°C, with the presence of a very small quantity of solid residue (less than 4%). An attempt was made to use the different kinetic models listed above to gain insight into the reaction mechanisms occurring in this complex sample. Pyrolysis tests were also carried out showing a yield of around 50 % in liquid and wax-like products. Changing conditions, especially temperature ramp rate and nitrogen flow had a significant influence over product distribution. High pyrolysis temperatures (>800°C) promoted the hydrogen formation.

While polyolefins devolatilize almost completely the pyrolysis of the plastic waste generates a residue due to the presence of other heterogenous materials. The final pyrolysis temperature exhibited a marked impact on the liquid and especially gas product distribution.

DESIGN OF BIOBASED UV CURABLE FORMULATIONS FOR 3D PRINTING

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In recent decades, there has been substantial growth in the development of polymeric materials sourced from renewable biological origins, primarily motivated by environmental concerns. Moreover, the depletion of oil, which is the primary carbon resource for polymer synthesis, has stimulated in-depth research into alternative sources that have a reduced environmental impact. This work focuses on biobased alternatives, specifically acrylated epoxidized soybean oil and polyglycerol-based acrylic monomers as VAT polymerization feeding materials.

In this study, two types of photocurable formulations were created: one set included acrylated epoxidized soybean oil (AESO) with varying weight percentages of biobased (meth)acrylated reactive diluents, while the other set comprised polyglycerol-based acrylic monomers. Reactivity characterizations were performed by Fourier transform infrared spectroscopy (FT-IR), photo-differential scanning calorimetry (photo DSC) and photo-rheology. Viscosity and mechanical properties were also tested through rheological measurements, dynamic mechanical thermal analysis (DMTA) and tensile measurements. DLP 3D printers were used to create complex structures.

AESO formulations showed high curing rate values, low gelification times (tgel) and viscosity values appropriate for DLP 3D printing. Considering these parameters formulations containing from 20 to 50 %wt of acrylated reactive diluents were used to print samples for mechanical analyses and complex structures to characterize printing process. Polyglycerol based formulations showed high FT-IR conversions (over 90%), high curing rate values and low tgel which made them suitable for DLP 3D printing. The prepared formulations were used to print complex structures to characterize the accuracy of the process.

Based on the reactivity and rheological assessments, the formulations developed in this study are suitable as feeding materials for DLP printing. The printed structures demonstrated precise detailing and well-defined surfaces, maintaining the characteristics outlined in the CAD model. In addition, mechanical analyses of AESO formulations revealed that objects incorporating isobornyl acrylate as a reactive diluent displayed favorable Young’s modulus values, enhancing structural stiffness.

PHOTOCATALYTIC DEGRADATION OF POLLUTANTS BY NANOMETRIC BIMETALLIC-MOF: NON-TOXICITY AND LOW ENVIRONMENTAL IMPACT

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Metal Organic Frameworks (MOFs) are porous crystalline materials with increasing interest in photocatalysis. Due to their porous structure, they offer a wide surface area and distribution of active sites. Manipulable chemical composition allows for the design of materials with specific photocatalytic properties. MOFs enhance the efficiency and selectivity of photocatalytic reactions, enabling new design opportunities for advanced catalytic systems. Functionalized with photoreactive groups or co-catalysts, they maximize performance and exploit specific wavelengths of light. They promise significant progress towards sustainable and efficient chemical processes.

The MOF was directly obtained from the solution via solvothermal synthesis. The synthesis was conducted at reflux in dimethylformamide (DMF) at 140°C for one hour. 2,6-naphthalenedicarboxylic acid served as the organic precursor, while bismuth salt acted as the metallic precursor. To obtain a bimetallic MOF, europium salt was added to the precursor solution at a 1:10 ratio with bismuth. To accelerate the synthesis process, a small amount of NaOH was added to the solution as a catalyst. This synthesis approach allowed for the production of a highly crystalline material with controlled composition in a short time and with high yield.

The synthesized MOF exhibits elongated nanometric morphology, enhancing its surface area for contact with pollutants. Notably, bismuth and naphthalene carboxylic acid precursors are non-toxic, while the low europium content minimizes environmental impact. Photocatalytic degradation tests were conducted at a concentration of 0.3 mg/mL of MOF nanoparticles. Results indicate the material has the capability to degrade 75% of the pollutant in solution, utilizing a low-power LED lamp. This underscores the MOF's potential as a photocatalytic catalyst for environmental applications, highlighting its promising role in sustainable pollution mitigation. The nanometric morphology enables increased surface contact, optimizing pollutant degradation efficiency. The non-toxic nature of bismuth and naphthalene carboxylic acid precursor elements further enhances material safety. Moreover, the minimal europium content ensures minimal environmental impact. These findings demonstrate the effectiveness of the synthesized MOF in addressing environmental challenges through photocatalytic degradation, paving the way for eco-friendly pollution mitigation strategies.

VALORIZING SCRAPS FROM THE LEATHER INDUSTRY THROUGH ADDITIVE MANUFACTURING: DIRECT INK WRITING AND NONPLANAR SLICING FOR PERSONALIZED PRODUCTS IN THE WATCH SECTOR

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The global leather market is expected to grow in the next years, with an estimated value of more than $400 billion in Europe by 2030 However, the leather industry generates different greenhouse gas emissions, volatile organic compounds, scraps and by products, e.g., tanned and untanned leather residues. Circular economy principles represent a potential way to use leather by products as secondary raw materials for new applications. This work aims to use leather residues as fillers in 3D printable epoxy based inks for customizable products in the fashion industry.

A flexible thermal curable epoxy resin was selected as the matrix for ink formulations containing 10 or 15% wt. of grinded leather filler with a granulometry >0.5 mm and 5% wt. of silica. The formulations were processed through a custom desktop size Direct Ink Writing (DIW) 3D printer with a pneumatic extruder and a plastic conic nozzle (1.6 mm diameter). The tensile properties of the formulations and the neat resin were tested on cast and 3D printed specimens following the ASTM D3039/D3039M 17 standard. Conventional and nonplanar slicing techniques were used to fabricate rectangular samples for surface roughness measurements assessing the staircase effect from 3D printing. A demo product was then fabricated to evaluate the printability of the inks.

The inks were successfully 3D printed, obtaining planar tensile specimens and rectangular planar and nonplanar samples. The tensile tests highlighted the reinforcing effect of the leather particles with minimal differences between cast and 3D printed samples confirming good printability. Using custom Grasshopper slicing definitions reduced the staircase effect from DIW 3D printing. A demo product for the watch sector, i.e., a customizable watch strap, was designed and fabricated as a proof of concept for future applications with custom nonplanar patterns and ink formulations.

The shape retention before the thermal curing was obtained by combining the shredded leather and silica weight content in the inks, achieving good extrudate processability. Combining these ink formulations with nonplanar slicing for the fashion sector can pave the way for new circular economy practices, reintroducing leather scraps in the same loop and reducing the need for virgin raw materials.

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MOLECULAR PACKING OF THIOPHENE DERIVATIVES: THE ROLE OF THIOCARBONYL-DIHALOGEN INTERACTIONS

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The molecular organization of π conjugated compounds plays a crucial role in the performance of organic electronic devices. The development of new methods devoted to control the molecular arrangement in the solid state is essential for the technological progress towards highly efficient and energy efficient devices. In this context, the terminal electron directing functional groups of organic linear semiconductors can be exploited to promote intermolecular interactions with solid state additives. With the aim of advancing fundamental knowledge in this field, we have investigated the formation of crystalline adducts induced by intermolecular interactions between the terminal electron withdrawing groups of π conjugated compounds and di iodine molecules.

Representative examples of thiophene based building blocks containing rhodanine functionalities were synthesised, and their ability to form crystalline adduct s with molecular I_2 was in vestigated. The obtained crystals were characterized by single crystal X ray diffraction analysis and Raman spectroscopy. Computational studies were performed to gain insight into the nature of the interaction between the exocyclic rhodanine thiocarbonyl (C=S) and diiodine. Finally, single crystal junction devices were used to evaluate the electric current of the bulk material.

Prepared compounds joining a 2,2' bithiophene moiety and a rhodanine ring form adduct s with I_2 through charge transfer (CT) from the sulphur atom of the thiocarbonyl unit. Derivatives containing unmodified rhodanine lead to an adduct with a 1:1 ratio of π molecule dihalogen. In contrast, modified thiorhodanine featuring two thiocarbonyl units promotes the formation of an infinite polyiodine network. Electrical measurements performed on the crystal of bithiophene rhodanine as well as on the corresponding iodine adducts show a higher current flow in the latter.

The mono thiocarbonyl compound was synthesized by Vilsmeier reaction followed by Knoevenagel condensation starting from 2,2' bithiophene. The resulting di thiocarbonyl derivative was prepared by treatment of the former with Lawesson 's reagent. The introduction of a second thiocarbonyl unit introduces a second point of interaction as well as an increase in the electron donating character towards the iodine molecule. Our preliminary results show that the thiocarbonyl sulfur in the thiophene based compound can act as an efficient coordination site for diiodine without undergoing undesired side reaction s on the thiophenes. The enhanced current flow suggests that diiodine may be a promising solid additive for modulating molecular packing during the film deposition process.

HIGH PERFORMANCE GREEN COMPOSITES WITH GRAPHENE OXIDE-COATED DWARF PALM FIBERS

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Substituting a substantial portion of bioplastics with inexpensive natural fillers stands out as a promising alternative for cutting manufacturing costs, while valorizing non-edible biomass. Despite efforts in producing green composites, the creation of high performance/functional materials from natural sources remains relatively rare, thus posing a current challenge. Coating natural fibers with graphene oxide (GO) could be a successful strategy not only to improve fiber-matrix interfacial adhesion but even to provide green composites with emergent properties, such as electrical conductivity.

Poly(butylene adipate-co-terephthalate) (PBAT) was selected as a matrix. GO was synthesized via Tour's method. Natural fibers were achieved from Chamaerops humilis stalks (CHS) waste biomass, plasma-treated in different conditions and poured into GO aqueous suspensions to achieve GO-coated fibers. PBAT containing 50% of either pristine or plasma-treated CHS, with or without GO-coating, were then prepared by hand lay-up and compression-moulding at 145°C for 2 minutes. The materials were characterized by morphological, physicochemical, mechanical, and electrical analyses.

Incorporating green fillers resulted in a notable enhancement of mechanical stiffness and resistance, albeit with a trade-off in toughness and ductility. Nevertheless, plasma-treated fibers ensured mechanical properties higher than raw CHS. The introduction of nanocarbons goes a step further in boosting mechanical performance, occasionally giving rise to emergent properties such as electroactivity. Among the samples, composites containing 50% GO-coated CHS plasma-treated at 120 W for 2 minutes outperformed, leading to observed increments of 500%, 150%, 120% and 110% in elastic modulus, tensile strength, ductility and toughness, respectively. Electrical conductivity, always ranging in the order of 10-6 S/m for composites containing GO-coated fibers, proved to be scarcely affected by plasma-treatment of fibers.

The fiber-matrix interfacial adhesion is the crucial challenge for improving all the ultimate properties of green composites. This aspect can be tuned and improved via coating the fibers with amphiphilic and robust GO. Additionally, natural fibers have the potential to serve as templates for both polymers and nanocarbons, guiding the latter towards the formation of a percolation network, even at low loadings, to create high-performance, multifunctional materials that significantly reduce raw and technological costs while offering environmental benefits.

This study was carried out within the MICS (Made in Italy - circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) - MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 - D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Uion nor the European Commission can be considered responsible for them.

PHYSICAL, MORPHOLOGICAL, AND MECHANICAL CHARACTERIZATION OF RECYCLED HYBRID NON-WOVEN MATS AS A CONTINUOUS FIBROUS REINFORCEMENT FOR NOVEL ECO-SUSTAINABLE PMMA THERMOPLASTIC COMPOSITES FABRICATION

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Nowadays, global objectives have given special attention to sustainability and circular economy in every sector, such as the composite industry. Therefore, the popularity of thermoplastic composites reinforced with recycled non-woven fabrics has been intensified for lightweight material fabrication. Particular attention has been given to hybrid tissues obtained from recycled Glass and Carbon fibers. In this paper, primarily the properties of dry TNT made from recycled Glass (GFs) and Carbon fibers (CFs) were evaluated. Afterward, these mats were impregnated with two different types of Elium resin (Arkema Co.) and were utilized to fabricate thermoplastic composite via vacuum infusion system in order to distinguish better impregnation. Finally, the polymeric composites were characterized from physical, morphological, and mechanical points of view.

ELIUM® C 040 and ELIUM® 158 O were purchased from Arkema Co. with peroxide polymerization using two various components, BENZOCLEAN and PERKADOX. CarbonTask Co. supplied GF/CF non-woven fabrics. In the first phase, dry hybrid GF/CF non-woven mats were analyzed to indicate their areal density, morphology, and tensile behavior. Density measurements were performed with METTLER TOLEDO Balance for 4cm^2 samples. Tensile analysis of dry hybrid non-woven mats was done by Zwick-Roell Z10 machine longitudinally and transversally. In the second experimental phase, dry hybrid GF and CF non-woven reinforcements were impregnated with two diverse types of Elium resin to produce thermoplastic composites via vacuum infusion method. At last, the composites were cut and examined to indicate their morphology, tensile characteristics, and flexural properties.

As dry non-woven mats were analyzed mechanically, it was revealed that due to the CF content enhancement, the mechanical performance of the non-woven fabrics was improved. GFs and CFs were distributed randomly through the non-woven fabrics. In the last phase of the experimental work, the fabrics will be impregnated with two kinds of PMMA resins with various viscosity to investigate higher reinforcement content with superior mechanical properties. Tensile properties, flexural behavior, and morphological observations will be demonstrated.

In this work, hybrid recycled non-woven mats based on GF and CF were impregnated with two different kinds of Elium thermoplastic resins (Arkema Co.) to investigate the composite fabrication process and the corresponding properties. The focus of the project in the next step is to refine the vacuum infusion method for composite production, an autoclave system to maximize vacuum pressure will be utilized. Another option is to fabricate composites through Resin Transfer Moulding (RTM).

STUDY OF POTENTIAL BIOLOGICAL RECYCLING THROUGH ANAEROBIC FERMENTATION OF PHBV BLENDED WITH BIOPLASTICIZER

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Poly(hydroxybutyrate-co-valerate) (PHBV), a member of polyhydroxyalkanoates (PHAs) is emerging in the bioplastics market and is used in fields like packaging and biomedicine. Its mechanical properties need to be improved by the addition of plasticizers to overcome its processing limitations. One possible route for recycling could be the bacterial fermentation of the materials to obtain carboxylates that can potentially be used as new raw materials in the production of PHAs.

PHBV was compounded with a newly synthesized green plasticizer, glycerol trilevulinate (GT), at 0, 2.5, 5, and 10 % by weight (PHBV, PHBV2.5GT, PHBV5GT, and PHBV10GT, respectively), and filaments suitable for 3D printing were produced. The thermal properties of the compounds were studied by differential scanning calorimetry as a function of plasticizer. Ground materials were utilized for solid particle fermentation (SPF) and fermentation after hydrolyzation by thermal-alkali treatment (TAT) of PHBV10GT. During the fermentation of PHBV+GT, in mixed bacteria culture under anaerobic mesophilic conditions, volatile fatty acid (VFA) production was monitored by gas chromatography.

The addition of increasing amounts of plasticizer resulted in a reduction in the glass transition (Tg) and melting temperatures (Tm). Fermentation after TAT occurred within a few days, with the conversion of crotonate to mainly acetate and butyrate. In contrast, SPF continued for six months, with increasing amounts of VFA produced.

Lower T_g and T_m allowed extrusion at lower temperatures, limiting thermal degradation. Hydrolysate concentration influenced the fermentation, finding optimal conditions at 10 gCOD/l, while no VFA was produced at 20 gCOD/l, suggesting that the bacterial metabolism was inhibited. It was also found that for SPF, the amount of plasticizer in the material affected the VFA production.

REMOVAL OF METHYL ORANGE AND PHARMACEUTICAL COMPOUNDS FROM WASTEWATERS BY COPPER-MODIFIED HEMP FIBERS

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Water pollution is regarded as a dangerous problem that must be resolved immediately. Among the pollutants, dyes and emerging pharmaceutical drugs have received widespread concern. The use of synthetic adsorbents is limited due to their high cost and regeneration. So, novel green adsorbents have been explored to remove different classes of pollutants from wastewater.

Hemp fibres (HF) were supplied by Nafco Company (Naples). NaOH in pellet form, $Al(NO_3)_3$*$9H_2O$, NH_4OH, Methylene orange (MO) and all the pharmaceutical drugs were purchased from Sigma Aldrich while HCl solution 37% v/v, NaCl, $MgCl_2$, $CaCl_2$ and KCl were purchased from Carlo Erba Reagents. Hemp fibres were modified with AlOOH groups through sol-gel methodology followed by copper oxide precipitation. MO adsorption tests were carried out in batch conditions by changing initial concentration, pH, temperature and ionic strength. Regeneration tests were even carried out.

Firstly, the adsorption capacity of Cu-modified hemp fibres was compared with raw hemp fibres. Then, parameters such as contact time, pH (2-12), temperature (20-80°C), initial concentration of dye (50-300 ppm), and presence of salts were varied and their effects on the adsorption recovery of methyl orange were evaluated. The data proved that the adsorption kinetics reached equilibrium within a few hours. The experimental data were fitted through a pseudo-second-order model while the Langmuir model well fit the adsorption data with a q_m=338.98 mg/g. Moreover, the produced adsorbent showed high selectivity and great performance in removing anti-inflammatory drugs with a removal efficiency of about 99% for Piroxicam and about 49 % for Diclofenac Sodium Salt.

Compared to raw HF, the presence of Cu improves the adsorption of MO (from 4% for raw HF to 98.9% for Cu-HF) due to the formation of electrostatic interactions with the functional groups of MO. The dye adsorption is concentration-dependent due to the increase in driving force while an acidic medium favored the removal of anionic dye. The presence of cations can alter the surface property and thus can influence the adsorption of MO. The positive ΔH proves that the process is exothermic. Besides the generation of OH bondings and electrostatic interaction promotes the removal of different pharmaceutical drugs. So, it is demonstrated the adsorption efficiency towards different pollutants of a novel, inexpensive, and sustainable composite material obtained from agro-waste resources.

ADVANCED INORGANIC CONSOLIDANTS FOR CARBONATE ROCKS PRESERVATION

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Among the various issues involved in the preservation of historical and cultural artifacts, the consolidation and protection of carbonate rock artifacts has always played a pivotal role. A common strategy is based on the treatment with ammonium oxalate/oxamate and diammonium phosphate. This limited choice of compounds is often used to consolidate this kind of lithotypes, although they have significant limitations such as poor water solubility and the formation of numerous metastable phases, respectively. The synthetic functionalization of these compounds allowed us to overcome these issues and increase the consolidating performance of the resulting ionic compounds.

Several innovative consolidants have been synthetised and fully characterized by microanalytical, structural, and spectroscopic means. The obtained compounds were applied to stone mock-ups and analysed using various techniques such as SEM microscopy, mercury intrusion porosimetry, X-ray diffraction, and NIR spectroscopy. In addition, variations in hydric, structural, colorimetric, and rugosimetric properties after the treatment were evaluated. The chemical nature of the synthesized compounds and their interaction with the stone were theoretically investigated by DFT calculations.

Over the past decade, five innovative consolidating agents have been developed. Each compound successfully infiltrated the stone's crack network, leading to precipitation in place. This resulted in the restoration of adhesion between stone particles and mitigation of degradation, minimizing observable effects such as surface roughness and material loss.

The role of chemistry has always been essential in the development of new materials for the protection and restoration of stone artifacts of archaeological and cultural heritage interest. Our capability in chemical synthesis, combined with our expertise in lithotypes, has significantly expanded the range of compounds identified as potential consolidating agents.

SYNTHESIS AND CHARACTERIZATION OF INORGANIC SILICA-BASED COATINGS TO PROTECT CULTURAL HERITAGE TEXTILES

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This paper presents a methodological framework for the synthesis and characterization of inorganic silica-based coatings designed to protect cultural heritage textiles, employing a multistep procedure. The synthesis involved the application of Tetraethoxysilane precursor at different concentrations to develop coatings on textile samples, with dibutyltindiacetate (DBTA) serving as a polycondensation catalyst for the sol-gel reactions. The interplay between catalyst presence, the number of coating layers applied to cotton fabrics, and their impact on diverse textile properties was explored.

Tetraethylorthosilicate (TEOS, ≥ 98%) was hydrolyzed in the presence of ethanol and HCl 0.1 M to obtain two TEOS solutions (0.03 M and 0.3 M) that were applied following a multistep procedure (1 to 6 layers) on scoured and bleached cotton fabrics (200 g/m^2). After drying (90°C for 5 min), treated samples underwent a last layer application of DBTA ethanolic solution (8% v/v on TEOS amount) and were finally cured (160°C for 5 min).

Infrared spectroscopy on treated fabrics confirmed the presence and chemical composition of inorganic silica layers whose morphology was investigated by scanning electron microscopy. Furthermore, the thermo-oxidative characteristics and abrasion resistance of sol-gel treated cotton fabrics, along with the durability of the coatings following multiple washing cycles, were examined. Specifically, both silica coatings exhibited strong adhesion to cotton fabrics, with the higher silica concentration correlating with enhanced thermal stability and durability of treated fabrics. Moreover, an improvement in abrasion resistance was observed for both precursor concentrations in the presence of the catalyst.

Experimental results highlighted the influence of inorganic multi-layered coatings on textile properties. In particular, the interaction of silica layers with both the cotton fibers and subsequent layers strictly affects the adhesion strength of the coating, firstly by silica particle diffusion into the fabric texture, then increasing the layer numbers, by covalent bonds between TEOS layers. These experimental outcomes underscore the effectiveness of tailored sol-gel materials in protecting and conserving cultural heritage textiles.

INTEGRATING 2D MATERIALS INTO MESOPOROUS FILMS, AN ADVANCED FUNCTIONAL PLATFORM

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2D layered materials, which have a layered structure similar to graphene, have attracted much attention because they have disclosed revolutionary new properties. The fabrication of advanced multifunctional materials whose properties are governed by the nanoscale requires the ability of mastering complex systems and related synthesis processes. The new generation zero-dimensional materials, such as carbon dots, provide the necessary functional properties that however need to be integrated into nanosystems of different scales. Two-dimensional materials such as graphene, boron nitride, WS_2 and $SnSe_2$, have been used to obtain heterostructures with highly controlled properties upon integration in mesoporous ordered titania films. Supramolecular self-assembly techniques, governed by weak forces during the evaporation of the solvent, allow the integration of nanomaterials into complex structures. Mesostructured materials are an example of such self-assembled materials that can host 2D materials without the disruption of the mesophase. The fabrication of devices capable of performing functions at different scales or through synergy due to the formation of nano-heterostructures can be, therefore, achieved through a pre-programmed self-organization. The 2D materials-mesoporous films heterostructures have shown to increase the photocatalytic performances of the system.

DEVELOPMENT AND CHARACTERIZATION OF COST-EFFECTIVE 3D BIOPRINTABLE HYDROGELS

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The field of bioprinting has seen significant advances in the processing of cell-loaded hydrogel structures. Several researches were limited to the use of bioinks supplied by printer manufacturers, often very expensive. This activity proposes the development of cost-effective 3D printable hydrogels using natural and biocompatible polymers (sodium alginate, xanthan gum and bovine gelatin) for pre-clinical medicine.

In this study, two new different hydrogel-based bioinks were studied, and compared with a commercial expensive bioink formulation, sold by the same manufacturer of the bioprinter used for the experimental work (Cellink Inc, Sweden).

The first hydrogel was based on sodium alginate (Sapore Puro), tested at concentrations of 2, 3, 6, 8 and 10% (w/v), prepared in distilled water at room temperature. A CaCl2 (Carlo Erba Milan) solution (80 mM) was used as cross-linking agent. The second hydrogel was based on xanthan gum, in the commercial version for food use as ThickenUp Clear (Nestlé, Vevey, Switzerland), and gelatin from bovine skin type B (Sigma-Aldrich, St. Louis, USA). The gelatin has been dissolved in distilled water using magnetic stirring at 900 rpm at 60°C, during which Xanthan Gum was added. Rheological and morphological characteristics of the inks have been evaluated by using a rheometer, scanning electron microscope and inverted microscope.

In conclusion, Alginate-10 % (w/v) and xanthan gum/2.4 % (w/v)-gelatin/6% (w/v) based formulations were found as the best concentration when the cell suspension was added to the gel. The work highlights the potential of these 3D printed constructs as frameworks in pre-clinical medicine for their easy printability and cell growth.

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ADVANCE IN LIPOSOMAL NANOFORMULATIONS: TARGETING NLRP3 INFLAMMASOME FOR FATTY LIVER DISEASE TREATMENT

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The chronic inflammation plays a pivotal role in the progression of Non-Alcoholic Fatty Liver Disease (NAFLD) which can also aggravate towards Non-Alcoholic Steatohepatitis (NASH), cirrhosis and hepatocellular carcinoma. The NLRP3 inflammasome mediates the interaction between the inflammatory microenvironment and immune cells whose dysregulated activation promotes immunosuppression, cancer, and metastases. Targeting macrophages by inhibiting NLRP3 inflammasome activation holds therapeutic promises for avoiding NAFLD progression. MCC950, a NLRP3 inhibitor, faces limitations such as short half-life and inadequate targeting, which could be addressed through nanocarrier encapsulation. Liposomes (LPs), versatile and biocompatible nanovectors, allows to deliver various compounds or nanoparticles (NPs). Carbon Dots (CDs), luminescent NPs with easy surface functionalization and high biocompatibility, have emerged as imaging tools for monitoring biological processes. Here, polyethyleneglycol (PEG)-LPs (co-)loaded with MCC950, and luminescent CDs were prepared to obtain optically traceable nanovectors for selectively inhibiting the NLRP3 activation in macrophages. The nanoformulations were synthesized via microemulsion approach starting from a lipidic mixture and PEG to enhance drug loading (DL%). Subsequently, they were conjugated with an anti-Frizzled1 antibody, overexpressed on the macrophages membrane, to achieve targeted nanocarriers. A comprehensive physical-chemical characterization was performed to investigate their morphology, colloidal stability, and optical properties. In vitro and in vivo studies were also carried out to assess the efficacy of these novel LP-based formulations as therapeutic agent to target activated macrophages. The LP-based formulations resulted characterized by monomodal size distributions, good colloidal stability, satisfactory DL% and peculiar optical properties. The presence of the anti-Frizzled1 antibody on the surface has been been assessed qualitetively by ATR FT-IR and quantified with a fluorescent secondary antibody. In vitro studies demonstrated high biocompatibility, enhanced cellular uptake and efficacy of the targeted nanoformulation to dampen down the inflammasome activation in macrophages. Finally, an in vivo pilot study demonstrated the reduction of hepatic inflammation and the modulation of the fibrotic progression of steatosis upon treatment with the targeted nanoformulation. The reformulation of MCC950 in LPs emerges as a promising strategy to substantially reduce the required drug doses. These specifically engineered LP-based systems offer the advantage of achieving comparable therapeutic efficacy with lower drug concentrations compared to the free form. This innovative approach holds considerable promise for enhancing the therapeutic potential of MCC950 in the management of inflammatory-driven diseases.

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MESOPOROUS SILICA MICROSPHERES CONTAINING TRANEXAMIC FOR HEMOSTATIC APPLICATION

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Uncontrolled bleeding is considered one of the most common causes of potentially preventable death either in the military or the civilian field. Early bleeding management is considered vital to decrease the risk of mortality. For this purpose, a novel hemostatic material based on mesoporous silica microspheres (MSM) and loaded with tranexamic acid (TXA) was developed to be used during first-aid procedures. The main goal was to achieve a material with large pores (>15 nm) as they present better hemostatic performances, and able to release TXA within an hour, according to the CRASH-2 trial to achieve maximum efficiency.
MSM were synthesized under acidic conditions using Pluronic P123 as a template agent, TEOS as a silica precursor and mesitylene as a swelling agent. TXA was loaded through the incipient wetness impregnation method using water as a solvent. A blood clotting time (BCT) test was performed to evaluate the hemostatic efficiency of the material, and a hemolysis assay was performed to evaluate its hemolytic activity. A preliminary in vitro release test was performed to verify the possibility of a fast release of TXA from the microspheres.
MSM with particle size of 1.5 -5 μm and pores diameter of 25 nm were successfully synthesized and loaded with TXA with a content of 4.7 %w/w. BCT tests indicated that the clotting time was significantly shortened by both samples with respect to control. Hemolysis assay showed that the material was hemocompatibile. The in vitro release showed that the material was able to deliver TXA within one hour.
This work aimed at developing a hemostatic material which combines the hemostatic ability of MSM with the antifibrinolytic activity of TXA, to be used in bleeding control. The synthesized material showed a good ability in inducing coagulation, as confirmed by the BCT test, as well as a rapid release of TXA, as indicated by the in vitro release test.
Based on the above results, it can be concluded that the proposed system is promising for the development of new hemostats suitable for bleeding control in emergency situations.

PRODUCTION AND CHARACTERIZATION OF INNOVATIVE BIODEGRADABLE FILMS BASED ON PBS/BVOH BLENDS

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The use of biodegradable polymers, at least for specific applications like food packaging, can represent a valid strategy to reduce the use of synthetic polymers. In the last years, crescent interest is devoted to the blending of biodegradable polymers for obtaining biodegradable films with tailored properties. In this work blends of Polybutylene Succinate (PBS) and Butenediol Vinyl-alcohol (BVOH) were prepared by melt-compounding. A preliminary rheological characterization of the systems was carried out, then blown films were produced and their mechanical, morphological and barrier properties were evaluated.
In this study PBS FZ91, supplied by Mitsubishi Chemical Corporation, with a melting temperature of 115°C and a glass transition temperature of -30°C and BVOH Nichigo G-Polymer™, designed for blown film extrusion, supplied by Mitsubishi Chemical Corporation with a melting temperature around 188 °C and a glass transition temperature of 75°C were used.
Thermogravimetric analyses highlighted higher thermal stability of PBS compared to BVOH, increasing the amount of PBS in BVOH-based blends led to an increase in the thermal stability of the blends. Differential scanning calorimetry (DSC) analyses have shown the presence of distinct thermal transitions related to both constituents confirmed the immiscibility of the two polymers. Rheological tests highlighted, over the investigated frequency range, a pronounced shear-thinning behaviour for all the PBS and BVOH blends, while with an increase in BVOH content, the blends tend to exhibit a solid-like behaviour. Fourier-transform infrared spectroscopy (ATR FT-IR) analysis identified possible interactions within the blends as revealed same shifts in characteristic absorption peaks of the pure polymers. Regard the films, water vapor permeability tests confirmed the excellent barrier properties of pure BVOH. The addition of BVOH in mixture with PBS allows to significantly reduce the permeability. In terms of mechanical properties, BVOH proved to be an extremely rigid and brittle material, the addition of PBS allows a partial recovery of the ductility of the systems up to a maximum elongation of 233% for the PBS/BVOH 80/20 blend. SEM analyses have revealed that the morphology conforms to that of immiscible mixtures. Oxygen permeability tests are now ongoing.

TUNING THE CORROSION RESISTANCE OF MAGNESIUM FOR IN VIVO APPLICATIONS BY BIPOLAR PLASMA ELECTROLYTIC OXIDATION

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Magnesium alloys hold significant potential as bone substitutes thanks to their optimal mechanical properties, matching those of cortical bone, alongside their intrinsic biodegradability. Nevertheless, the rapid corrosion of Mg in vivo frequently compromises this material's load-bearing capacity and triggers a pronounced inflammatory reaction, attributable to the abrupt increase in local pH. In this context, electrochemical surface modification processes such as Micro-Arc Oxidation (MAO) offer a promising route to control Mg corrosion, allowing to easily form protective ceramic coatings that facilitate bone regeneration at the implant site. Here, we present the tuning of novel pulsed bipolar MAO treatments on magnesium, aiming at improving the technique's suitability for prospective clinical applications.

The novel MAO treatments were applied to AZ31 magnesium alloy specimens using a simple siliconbased alkaline electrolyte. Several pulsed bipolar process conditions were tested along with various MAO setup configurations, and their effect on the coatings' cross-sectional morphological and chemical features was assessed by SEM-EDS. The corrosion resistance of the optimized samples was then tested by potentiodynamic polarization in various simulated biological media, while the coatings' adhesion to the substrate was evaluated by scratch testing.

The cross sectional structure of MAO coatings produced in bipolar conditions strongly differs between the samples based on the intensity and duration of the cathodic duty cycle: although all the coatings show a marked increase in thickness compared to those formed in matching unipolar conditions, with a sustained depolarization the formed oxide coating is mainly external, porous and discontinuous; conversely, as the cathodic phase becomes shorter, a clear bilayer surface appears, featuring a thin, porous outgrown layer coupled with a thicker internal one. The potentiodynamic polarization tests show a markedly reduced corrosion current density for the MAO coated samples featuring a thicker internal layer as compared both to more porous MAO and untreated AZ31 specimens. Moreover, the adhesion of the coatings appears to benefit from such high compactness at the oxide-metal interface.

The obtained coatings represent a possible combination of conventional PEO and oxygen diffusion phenomena, as highlighted by the peculiar "potato-like" structure of the inner, compact layer's deeper regions, potentially further boosting the oxide compactness and resistance against penetration of corrosion promoters from the surrounding environment. Such behavior is also suggested by the corrosion analyses and highlights the potential of applying bipolar MAO processes to produce significantly better lasting coatings for potential bone applications of magnesium and its alloys.

MECHANOSYNTHESIS OF NANOMATERIALS FOR BIOMEDICAL APPLICATIONS. QUO VADIS?

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Mechanochemistry that began with prehistory, is a green, quantitatively and rapidly way to run solid-state reactions. It has recently demonstrated to be versatile and successful in the preparation of several novel nanomaterials for biomedical applications by chemical transformations, usually accessible with difficulty or not at all in solution. Here, we present some of the recent achievements obtained by mechanochemistry at the "Chemistry of Micro and Nanostructured Materials" group at the University of Cagliari.

Natural extract - silica nanocomposites. Mixtures of natural extracts with fumed SiO_2, were milled in agate vials together with agate balls using a Pulverisette 5 planetary mill.

Iron trimesate Metal Organic Frameworks (MOFs). An innovative synthetic protocol for the preparation of an iron(III) trimesate MOF was carried out via mechanochemical route using a SPEX 8000 vibratory mill.

Natural extract - silica nanocomposites. After the milling process, the natural extracts were embedded in the SiO_2 matrix obtaining nanocomposites with high antioxidant and antimicrobial activity. The obtained nanocomposites were tested against a panel of microorganisms.

Iron trimesate Metal Organic Frameworks (MOFs). A MOF isostructural with MIL-100(Fe) was obtained. It showed better crystallinity and thermal stability, as well as higher surface area and pore volume than a commercial iron trimesate produced via electrochemical route. Moreover, we demonstrated the exceptional tailorability of the synthesis to the one-pot immobilization of biomolecules in the MOF structure during the synthetic process. An innovative bio-friendly mechanochemical route without adding solvents, over a mild pH range and with just 6 minutes reaction was developed in our laboratory to prepare enzymes - iron trimesate MOFs.

Mechanochemistry avoids the use of solvents and is a green, energy efficient, inexpensive, fast and easy to scale-up synthesis method compared to conventional routes. This is of main interest, especially in recent years, in which finding alternative and greener options urges to be addressed in every field of chemistry. Our results point-out that mechanochemistry is a valid alternative to classical synthetic methods.

PHYSICAL EXPANSION OF PCL-FOAMS LOADED WITH AQUEOUS EXTRACT OF HIBISCUS SABDARIFFA

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Hibiscus sabdariffa is a plant characterized by a high content of antioxidant molecules; its aqueous extract (karkadé) has potential health benefit during healing processes. However, this compound is particularly sensitive to oxidative and thermal degradation. In response to this issue, the present study proposes a new application for preserving karkadé extract inhibition power, while controlling its release rate. The concept involves trapping the karkadé extract in poly-ε-caprolactone foams, a biocompatible semicrystalline polymer widely used in the nutraceutical and cosmetic fields.

The aqueous extract was obtained using Rapid Solid Liquid Dynamic Extraction, processed at 20°C and below 10 bar. The entrapment of the aqueous extract occurred during the preparation of a 3 mg/mL PCL in acetone solution, which solidified obtaining a disk loaded with karkadé. Then, the disk was inserted into a mould and foamed at the pressure of 100 bar and temperature of 45°C, using CO_2 as a blowing agent. To test foams' biocompatibility, the foams were soaked in a liquid cell culture medium. Once reached the equilibrium, an aliquot of the sole liquid was withdrawn and put in contact with human skin cells (keratinocytes). Cell viability was evaluated by using MTS.

Karkadé was extracted with a final cumulative concentration of 195.0±4.6 g/L; furthermore, the reduction of the antioxidant inhibition power was 26.0±1.4 % after an observation time of 7.5 h. Foaming was conducted under optimized parameters (45°C, 100 bar and sorption for 1 hour), resulting in a foam density of 0.18 g/cm^3. Foam cell density of 2.04x10^4 cell/cm^3 and an average pore dimension of 51±22 μm were calculated after SEM observations. The loaded foams were characterized by a karkadé entrapment efficiency up to 97%, highlighting the efficacy of this encapsulation technique. Moreover, it was demonstrated that foams are biocompatible with human keratinocytes.

The release rate of karkadé was influenced by the establishment of a CO_2 concentration gradient within the polymer. To validate the scalability of this foams' innovation, a prototype resembling a patch infused with karkadé was designed. Release tests revealed that it is possible to tune the concentration of released karkadé by varying the CO_2 concentration gradient in PCL. Considering its biological validation, the patch prototype could find application in repairing skin damages. This work enabled us to assess the scalability of the high-pressure foaming process, laying the groundwork for a future investigation into the of biocompatible and lightweight mono-material patches.

AN INNOVATIVE AND SUSTAINABLE SYNTHESIS FOR THE PRODUCTION OF IRON OXIDES NANOPARTICLES COATED WITH BIOCOMPATIBLE POLYMERS FOR BIOMEDICAL FIELD

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Iron oxides nanoparticles allow the creation of non-toxic and low-invasive substances that have been used in the biomedical field for hyperthermia, drug targeting as well as magnetic resonance imaging (MRI). The methods of production, especially the most used wet chemical routes, use high temperature/pressure and have multiple steps of production to obtain the final product. Our group of research has developed an innovative, sustainable and patented one-step synthesis that works at ambient temperature and pressure allowing the production of pure magnetic iron oxide nanoparticles (MION).

The synthesis is based on an ionic exchange process between an anionic resin and a solution of ferrous chlorides ($FeCl_3$ and $FeCl_2$) in water. Coated MION are obtained by addition of biocompatible polymers, such as polyethylene glycol (PEG) and polyvinyl alcohol (PVA), which have been used in different concentrations. For each kind of polymer, three different syntheses have been carried out at different volume concentration: 25%, 50% and 75% for PEG in distilled water and 0.1%, 0.2%, 0.3% for PVA in distilled water. The resulting products have been analysed by several techniques such as X-Ray diffractometry (XRD), UV-Visible analysis, BET surface area measurements and scanning electron microscopy (SEM).

XRD analyses show the presence of a pure magnetic phase, perfectly matching the standard Fe_3O_4 ICSD pattern, together with the PEG/PVA signal. The suspension stability, analysed by UV-Visible Absorption, show very high stability especially for PEG coated MIONs characterised by a stable signal for several hours. This result is in agreement with SEM images where PEG-MIONs appeared better coated, more monodispersed and with smaller diameters, by increasing the polymer concentration (20-80 nm at 75% PEG).

The obtained results are very promising in term of obtaining iron oxides nanoparticles, properly coated by the biocompatible polymer, by a one-step and sustainable synthesis. The coated nanoparticles result stable when dispersed in water, ready to be used in MRI measurements to verify their usefulness in the biomedical field as non-toxic substances.

GELLAN GUM MICROPARTICLES FOR INTESTINE-TARGETED DELIVERY OF PROBIOTICS

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This study focuses on developing carriers for probiotic formulations to create innovative functional foods. Among biobased polymers, gellan gum was chosen for encapsulating probiotic microorganisms due to its widespread use as a gelling agent in various foods and as an agar substitute for microbiological plate assays. Additionally, gellan gum microparticles have demonstrated cryoprotective and gastroretentive properties.

Lactobacillus Fermentum was used as model probiotic for this work. Gellan gum microparticles were produced by electrohydrodinamic microdripping. Gellan gum powder was disselved in distilled water at different concentrations (0.5, 1, 1.25 %wt) by stirring at 90°C. Solutions were autoclaved and pumped throug a stainless steel needle (positive high voltage). Microparticles were directly collected in 20 mL of 1%wt $CaCl_2$ crosslinking bath (grounded). *L. Fermentum* was inoculated in De Man, Rogosa and Sharpe (MRS) broth and plated on MRS agar to determine colony-forming units (CFU). Bacterial suspensions were prepared determining OD600, centrifuged and resuspended in 1% wt gellan gum (GG1), to achieve probiotic loads of 10^6 CFU/mL (GG1-low) and 10^9 CFU/mL (GG1-high). GG1-low was re-incubated in MRS broth for 24 and 48h and stained with Syto9 fluorescent dye to assess bacterial growth inside the particles.

A 1% wt gellan gum solution was identified and tested for probiotic entrapment. Wet particle size distributions were systematically studied at an optimized flow rate (1 mL/h) and voltage (25 kV) to evaluate the effect of probiotic inclusion. Empty particles had a mean size of 250 ± 50 µm, while GG1-low (10^6 CFU/mL) and GG1-high (10^9 CFU/mL) had sizes of 300 ± 40 µm and 450 ± 100 µm, respectively. Plating of the particles showed high probiotic viability post-encapsulation. Plating of the crosslinking bath after filtration displayed at least 2-log units less CFU with respect the dripped ones, indicating high encapsulation efficiency.

The obtained particles exhibited a size range suitable for the food industry, and various concentrations of microorganisms were successfully trapped inside the hydrogel matrix. Re-incubation of GG1-low and Syto9 staining demonstrated the ability of probiotics to grow both inside and on the surface of the particles. Overall, the tested processes proved effective for directly encapsulating high probiotic loads and regrowing probiotics within the particles. The latter method may potentially be utilized to produce particles containing both high loads of probiotics and postbiotics in a single formulation.

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NANOSTRUCTURED SILK FIBROIN CARRIERS AS INNOVATIVE APPROACH FOR PULMONARY DRUG DELIVERY

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Silk fibroin (SF) represents a promising biomaterial suitable for drug delivery, due to his bio/cytocompatibility, chemical stability and mechanical properties. Recent studies demonstrated that inhaled administration of the thyroid hormone levothyroxine (L-T4) in an Idiopathic Pulmonary Fibrosis (IPF) model is able to resolve lung damage. Conversely L-T4 direct administration conflicts with L-T4 low solubility and stability; an efficient delivery system also complying with specific dimensional rules is thus required. Indeed, in the lungs particles between 2-10 μm are normally deposited in the tracheobronchial region, and particles of size 0.5-2 μm are deposited in the alveoli. Here we propose an innovative method for the synthesis of SF nanostructured carries (SFNC) with a high L-T4 loading efficiency, using $CaCO_3$ as template. As-prepared SFNC, suitable for diseases as IPF, are scalable to different varieties of drugs loading for the treatment of several pulmonary illnesses.

$CaCO_3$/L-T4 loaded particles were synthesized by mixing equal volumes of 0.1 M solution of $CaCl_2 \cdot 2H_2O$ and Na_2CO_3 in water and ethylene glycol (1:5, v/v) adding 0.02 M L-T4. As-prepared $CaCO_3$/L-T4 particles, were coated adding 0.5 % (w/v) of standard aqueous SF solution to the aqueous dispersion of $CaCO_3$/L-T4. Adsorbed SF has been crystallized for 30 min with a 50 % (v/v) water/methanol solution. To dissolve $CaCO_3$ template, the particles were treated for 30 min in 0.1 M EDTA in 0.4 M KOH. SFNC for fluorescence microscopy were prepared by labelling L-T4 and SF with fluorescein and B-rhodamine. SFNC were also characterized by SEM-EDX and DLS.

$CaCO_3$/L-T4 particles demonstrated high loading efficiency and stability, with a slight solubilization and aggregation tendency. The aggregates were constituted by primary particles with a diameter ranging around 1 μm, as confirmed by SEM and DLS analysis. After the $CaCO_3$ template removal, SFNC showed a comparable a morphological profile, with a global dimensional decrease. Larger aggregates ranged between 5 and 1 μm, while primary particles between 100 and 300 nm. L-T4 loading and the complete elimination of $CaCO_3$ template were confirmed by fluorescence microscopy and SEM-EDX analyses.

SFNC exhibited high drug loading efficiency, structural heterogeneity and nanostructured morphology. Those characteristics could be crucial to select the most suitable and effective sizes, accomplishing a high deposition rate in the appropriate lung districts. Moreover, once delivered, the hypothetical detaching of primary nanosized particles could definitely enhance drug release, bioavailability and therapeutic efficacy.

DESIGN AND FABRICATION OF DRUG-LOADED SILK FIBROIN MICROCARRIERS WITH TAILORED SIZE AND SHAPE FOR DRUG DELIVERY APPLICATION

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The design and development of drug delivery systems (DDSs) represent a crucial area of research in the pharmaceutical field. Micro/nanoparticles have garnered significant interest as DDSs, offering superior therapeutic performance compared to traditional delivery forms. Micro/nanoparticle carries can be prepared using synthetic and natural biodegradable polymers, such as silk fibroin (SF). SF possesses unique properties, such as biocompatibility and adaptability, making it an attractive material for drug delivery. This study focused on designing of SF-based microparticle systems. The goal is to optimize the synthesis of SF particles with controlled size and shape aimed at tailoring an efficiently controlled drug release.

A method and its optimized version were developed to prepare SF particles using a $CaCO_3$ template loaded with a model drug. SF was extracted from the cocoons of Bombyx mori. The particles were first synthesized by mixing aqueous solutions of $CaCl_2$ and Na_2CO_3, a fluorescein-labelled model drug and rhodamine-labelled SF at 800 rpm for 1 min. Subsequently, the method was optimized by carrying out a mixing of $CaCl_2$ and Na_2CO_3 in presence of ethylene glycol (EG) at increased reaction time and stirring speed. The resulting $CaCO_3$ particles were loaded and subsequently coated with SF, followed by methanol treatment. Finally, ethylenediaminetetraacetic acid (EDTA) was used to remove the $CaCO_3$ core. The two SF-particles systems were studied using optical and fluorescence microscopy, DLS, SEM and EDX.

In this study we have optimized a standard methodology for DDSs, obtaining SF microparticles that were able to encapsulate a model drug. We have demonstrated that the addition of EG during the synthetic process resulted in a particle size decrease. We obtained homogeneous $CaCO_3$ particles coated by SF with an average size of 1 μm. After EDTA treatment, EG-treated particles maintained their spherical shape. These results indicate that the optimized method offers an opportunity to improve the structural integrity of SF particles, positively influencing the delivery performance.

The first system was synthesized by a co-precipitation method. SEM images show particles consisting of spherical structure and about 5-6 μm in diameter. The second system was synthesized by coating the drug-loaded $CaCO_3$ particles with SF, obtaining a spherical structure with a diameter of 1 μm. After EDTA treatment, SF particles obtained by the standard method collapsed, while in the optimized method they maintained their spherical shape. Fluorescence analysis and EDX confirmed the successful encapsulation of the drug.

RAMAN-BASED TECHNOLOGIES FOR CANCER DIAGNOSIS AND THERAPY IN THE PHAST-ETN PROJECT

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The main objective of the PHAST-ETN action is to develop advanced photonic technologies for in vitro and in vivo cancer diagnosis and therapy monitoring for personalised medicine. Raman-based technologies have demonstrated their great impact on biomedical research, as the Raman spectrum provides a molecular fingerprint of any biological sample.
The aim of this study is to develop novel SERS-based optofluidic devices, in biological protocols consisting of surface functionalisation of metal-dielectric nanostructures for the detection and quantification of tumour biomarkers aimed at early cancer diagnosis through a liquid biopsy approach. This activity merges technologies dedicated to the synthesis of innovative nanostructures and/or SERS labels and surface biofunctionalisation, as novel technologies for the detection of tumour biomarkers.
The protocols were grouped into 5 categories and performance evaluation was conducted based on two parameters: detection abilities and applicability in body fluids.
Different types of SERS substrates were developed and tested, such as Au-Ag NPs grown on the glass substrate, as colloidal solutions, or on CaF_2 substrates.
The measurement of RNA-bases showed that the best LOD was achieved by AgNPs-LM colloidal solution produced by the Lee-Meisel approach. Two miRNAs, let7a and let7i, were successfully measured down to 10-8 M. Therefore, AgNPs-LM were dropped on the CaF_2 substrate and the label-free capture-based protocol was implemented. Two capture DNAs, complementary to each miRNA, were immobilized on the substrate by dropping a sample or an incubation of the substrate inside the sample. The second approach was more effective and resulted in the detection of capture DNAs and target miRNAs at 10-6M.
SERS measurement of nucleic acids, especially miRNAs, is an approach for the liquid biopsy application. It can be combined with many different simple protocols and conducted on various types of substrates, including PCFs. The main challenge to be addressed by the researchers is to design reproducible and sensitive SERS sensors.

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RE.MO.PACK - STUDY AND DEVELOPMENT OF AN INNOVATIVE RECYCLABLE MONOMATERIAL FILM AND ITS INTRODUCTION INTO THE FOOD PACKAGING PROCESSES

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The RE.MO.PACK project aims to identify mono-material structures for flexible packaging, made almost entirely from a single polymer, validated on technological systems in an operational environment. The project seeks to overcome the current issues in recycling multi-material films, by studying a more recyclable and circular packaging obtained through a process of high vacuum deposition of metal oxides on different polymeric films. Therefore, the film can achieve performance comparable to current multilayer structures while being considered mono-material, according to EU regulations.

This study aims to develop innovative mono-material structures with an optimized vacuum and atmospheric coating combination and to analyse their recyclability through a mechanical laboratory-scale recycling process. The analysed polyolefin-based films are subjected to grinding, extrusion with single or twin-screw extruders, pelletization, and production of dog-bone specimens via injection molding. The main characterisation techniques adopted are: tensile, thermomechanical (DMA), and rheological (MFI) testing, compositional analysis and scanning electron microscopy (SEM).

Results of the literature review as well as preliminary results of the properties obtained from the various characterizations will be presented through a comparison between the recycled material and the starting material from post-production flexible films.

A preliminary literature review shows the variability in the composition of the flexible polyolefin films, the collection infrastructure, and the complex sorting as the main factors affecting the materials' recyclability. Nowadays, most of these materials are sent to landfill disposal or energy recovery. This highlights the importance of redirecting demand for flexible packaging films towards recyclable solutions.

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