AMATS 2023

ABSTRACT BOOKLET

Monday, November 13th - LA3

DESIGNER DNA-BASED NANOMATERIALS FOR THERAPEUTIC DELIVERY

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Keywords: *DNA nanotechnology, self-assembly, drug delivery, gene therapy, liposomes, cardiac disease*

DNA nanotechnology is a unique synthetic tool for the reproducible preparation of biodegradable and tailored nanomaterials.[1] The fabrication process is programmable and robust as it relies on the accurate specificity of the Watson-Crick-Franklin base-pairing interactions. Remarkably, the dimensions and functionalities of these DNA-based constructs can be customized and precisely controlled at the nanoscale level, which is key for some biomedical applications. We have exploited these unique characteristics to obtain tailored DNA-based nanomaterials (DNS) for the delivery of therapeutic agents targeting cancer and cardiac diseases.

Regarding cancer, we have prepared a set of simple DNS with subtle structural modifications and investigated their overall capabilities as nanocarriers for chemotherapy by evaluating their biological stability, their cellular internalisation, their ability to trap the anticancer drug doxorubicin as well as their effect on the viability of cancer cells.

In relation to cardiac disease, we have developed DNS for gene therapy finely folded with precise sequences for the trapping of a specific microRNA (miR) whose overexpression is associated to cardiac aging. We have studied the efficacy and specificity of miR capture by DNS *in vitro* and in cardiomyocytes of human origin obtained through iPSC differentiation.[2]

We are also working on hybrid carriers by adapting our DNS to interact with synthetic liposomes as stimuli-responsive containers [3] or with synthetic polymers through innovative bio-conjugation strategies with the aim of maximising the biological performance of our nanomaterials.

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TUMOR-TARGETED MESOPOROUS SILICA NANOPARTICLES AS VEHICLES OF MIR-200C-3P FOR BREAST CANCER TREATMENT

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Keywords: *mesoporous silica nanoparticles, breast cancer, microRNA, therapy.*

Breast cancer remains as the leading cause of cancer-related death in women worldwide [1]. In this context, microRNAs have emerged as potential therapeutic targets to modulate some dysregulated signalling pathways in tumour cells. Specifically, miR-200c-3p is a well-known tumour suppressor by inhibiting the progression and metastasis of breast cancer through downregulating ZEB1 and ZEB2 [2]. Nevertheless, microRNAs have a poor pharmacokinetics profile, which cause serious limitations for in vivo applications. Based on the above, we proposed the use of mesoporous silica nanoparticles (MSN) as targeted vehicles to carry and deliver miR-200c-3p in breast cancer cells [3]. We designed, synthesised and validated the nanodevice, demonstrating its biocompatibility as well as their ability to escape from endosomes/lysosomes and inhibit tumorigenesis, invasion, migration, and proliferation of tumour cells in vitro. Moreover, tumour targeting and effective delivery of miR-200c-3p *in vivo* are confirmed in an orthotopic breast cancer mouse model, and the therapeutic efficacy is also evidenced by a decrease in tumour size and lung metastasis, while showing no signs of toxicity. Overall, our results provide evidence that miR-200c-3p-loaded nanoparticles are a potential strategy for breast cancer therapy and MSN based nanodevices are safe and effective system for tumour-targeted delivery of microRNAs. The results of this work gave a publication in a scientific journal [4].

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AMatS
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Self-assembly of amphiphilic block copolymers based on 2,6-diaminopyridine for application in nanomedicine

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Keywords: *amphiphilic block copolymers, self-assembly, drug delivery, microfluidics, polymerization-induced self-assembly (PISA), Pd-nanosheets, photothermal therapy.*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Amphiphilic block copolymers (BCs) are able to self-assemble in aqueous solutions into different structures, such as micelles or vesicles, whose morphology and size depend on the length of the blocks, their chemical structure, the hydrophobic/hydrophilic balance and the method of preparation. These nanostructures can be employed for biomedical applications since they are able to encapsulate precursors of thermal transductors or bioactive molecules.

The synthesis of different amphiphilic BCs containing pendant 2,6-diaminopyridine (DAP) units is reported in this work, as well as the study of their self-assembly in water by the co-solvent method, [1] microfluidics [1] and under PISA conditions. [2] The size and morphology of the resulting polymeric nanoparticles (NPs), influenced by the polymer architecture and the experimental conditions, have been determined mainly by TEM and DLS. In addition, their cytotoxicity has been studied in several different cell lines. Moreover, Pd-polymeric NPs were internalized on different cell lines and their potential application in photothermal therapy has been evaluated. Additionally, the potential of these polymeric NPs as drug nanocarriers has been explored by encapsulating model fluorescent probes and drugs. DAP units are able to bind thymine moieties by molecular recognition through three hydrogen bonds, since DAP is an adenine analogue. Thus, thymine cross-linkers have been incorporated to prepare supramolecular cross-linked polymeric nanoparticles, which constitutes a more versatile approach than covalent chemistry.

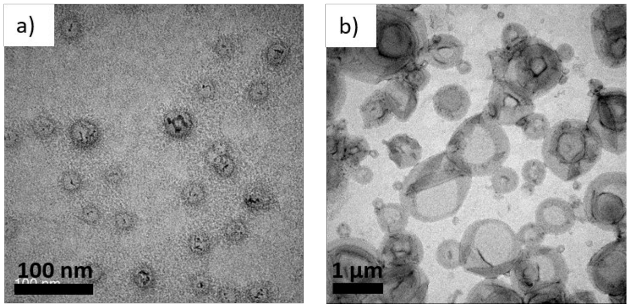

Figure 1 – TEM images of some representative examples of polymeric nano-objects prepared by a) microfluidics and b) PISA.

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DEVELOPMENT OF NEW NANOMATERIAL-BASED DETECTION SYSTEM FOR RAPID SENSING OF PATHOGENS

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Keywords: *nanoporous anodic alumina films, P. aeruginosa, sensing, nanomotors.*

Infectious diseases represent one of the most important health problems causing around 25,000 deaths in Europe every year and being the second cause of mortality according to the World Health Organization. Late or incorrect diagnosis of these diseases can lead to inadequate treatment and complications of the disease. In this scenario, the development of fluorogenic probes based on oligonucleotide capped nanoporous anodic alumina films [1] for specific and sensitive detection of *Pseudomonas aeruginosa* DNA and *P. aeruginosa* resistance genes like $\text{bla}_{\text{oxa-48\_like}}$ are being carried out. The probe consists of anodic alumina nanoporous films loaded with the fluorophore rhodamine B (RhB) and capped with oligonucleotides bearing specific base sequences complementary to genetic material of *P. aeruginosa*. Oligonucleotide molecules onto nanoporous films block the pores until specific DNA of *P. aeruginosa* and DNA of *P. aeruginosa* resistance genes like $\text{bla}_{\text{oxa-48\_like}}$ are present in the medium, resulting in RhB delivery, that is detected by fluorescence measurements. The sensing assays are optimized for reliable fluorescence signal reading. Furthermore, the development of nanomotors for *P. aeruginosa* detection is also being explored. Those are based on Janus-type particles with a mesoporous silica face and a platinum face [2]. The platinum nanoparticle will be self-propelled by H_2O_2 catalysis, while the mesoporous nanoparticle will recognize DNA of the bacteria. This binding will change the motion of the particle, and that change in motion will allow detection of the pathogen.

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ANTIMICROBIAL MATERIALS BASED ON POLYOXOMETALATE-PEPTIDE COVALENT HYBRIDS

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Keywords: *peptide, polyoxometalate, ring-opening polymerization, self-assembly, antimicrobial*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

The cumulative effect of emerging antimicrobial resistance (AMR) to traditional antibiotics and the lack of effective replacement treatments has translated into the urgent need to identify alternative microbiocidal agents. With this objective, in our group we work under the hypothesis that by combining elements with different mechanisms of antimicrobial activity in the same material, we could favour synergic effects and prevent the appearance of AMR.

On one hand, POMs represent a class of anionic molecular metal oxides, which show excellent thermal and redox properties. It has been shown that certain POMs exhibit antimicrobial activity mainly based on their ability to induce the production of reactive oxygen species, although other mechanisms have been reported.[1] On the other hand, antimicrobial peptides (AMPs) have received increasing attention because of their rapid action and broad-spectrum antimicrobial activities. AMPs are usually formed by sequences combining hydrophobic and cationic amino acids which allows them to interact with and disassemble microbial membrane.[2]

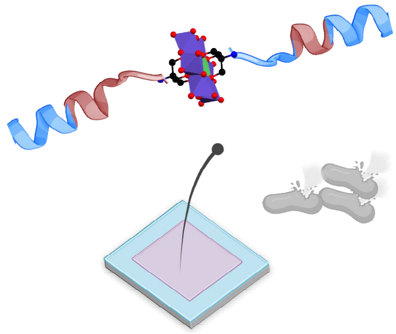

Figure 1 – Schematic representation of a POMlymer and its antibacterial activity as a coating (Created with BioRender.com)

We have recently introduced POMlymers as covalent POM-polypeptide hybrids prepared through the ring-opening polymerization of amino acid *N*-carboxyanhydrides initiated by an amino group on the POM (Figure 1).[3] By using apolar and positively charged amino acids we can mimic the main structural parameters of antimicrobial peptides. We have characterized the self-assembly behaviour of the POMlymers, and have demonstrated that these covalent hybrids exhibit superior antimicrobial and antibiofilm activity compared to the ionic hybrids, and POM and polypeptide separately, providing insight on the dual role of ROS generation for biofilm formation.[4]

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ADVANCED FUNCTIONAL POLYMERIC NANOCOMPOSITES FOR POLLUTED WATER REMEDIATION

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Keywords: *pesticides, bacteria, copper, silver, catalysis*

AMatS3.- Smart materials with advanced functionalities.

Providing access to potable water to the entire population is a global issue of utmost relevance. The United Nations (UN) prevision is that about half of the entire world population will live in water-stressed areas by 2025[1]. Advanced functional materials have arisen in the last years as promising new approaches to clean polluted water. For instance, polymeric nanocomposites have been successfully developed for the remediation of oil spills[2] or nitrates-polluted water[3]. However, most of these approaches involved the adsorption of the pollutant, being the materials sometimes limited to one use and then potentially becoming a hazardous waste. Alternatively, the degradation or inactivation of the pollutants with reusable advanced functional materials is a desirable approach, avoiding the generation of wastes and increasing the remediation capability of the materials. An example of this approach was the development of highly porous melamine foams functionalized with silver nanoparticles, which showed a remarkable bactericide capability even in filtration setups[4]. Unfortunately, the proposed production route involved hazardous solvents, being necessary the development of greener production approaches for the safe production and use of these materials. Another dangerous pollutant that has been possible to degrade by using metallic nanoparticles, in this case copper, is the chlorpyrifos, a recalcitrant pesticide with acute toxicity for the aquatic ecosystem, birds, and mammals, including humans. However, the use of free nanoparticles in the environment is inadvisable due to safety concerns. Herein, new approaches for the development of bactericide melamine foams functionalized with silver nanoparticles following green production routes, as well as of copper nanocomposite electrospun fibers capable of addressing chlorpyrifos pollution[5] are presented. On the one hand, the synthesis pathway of silver nanoparticles into melamine foams and the influence of the processing parameters were optimized to phase out the 100 % of polluting and dangerous solvents while maximizing of silver transfer. A deep study of the morphological and chemical changes of the synthesized silver nanoparticles successfully demonstrated that water could be used as the only solvent for obtaining active melamine foams. On the other hand, the immobilization of copper nanoparticles into a polycaprolactone matrix via electrospinning was demonstrated to be a very effective method to retard air and solvent oxidation and to ensure constant catalytic activity for the remediation of chlorpyrifos-polluted water in the long-term. Interestingly, the degradation process was independent of the light conditions (i.e., not photocatalytic), expanding the application environments (e.g., groundwaters).

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Using Polyoxometalate-Ionic Liquids as Multifunctional Antifouling Coatings and Water Purification Solutions

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Keywords: *polyoxometalate, ionic liquid, antimicrobial, water purification, biodeterioration*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Organo-functionalization of polyoxometalates (POMs) represents an effective approach to obtain diverse structures and arrays of practical materials with tailored surface chemistry, charge, polarity, and redox properties.[1] POMs also possess excellent biological activity: they can cross lipid membranes, interact with proteins and are producers of reactive oxygen species. Together, this combination of physicochemical properties with biological activity makes them suitable for a variety of end uses as functional materials for environmental applications. Here I will show how we have been applying POM-ILs as multifunctional coatings to prevent biodeterioration of stone-based cultural heritage objects and architectures [2-5], and discuss their application as universal pollutant removal materials.[6,7]

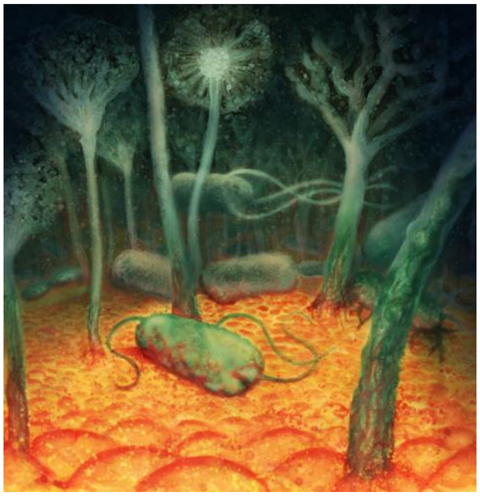

Figure 1. Modular POM-ILs act as precision biocides that prevent microbial colonization of surfaces.

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Scaffolding Silica Aerogels for Environmental Purposes: Thermal insulation and Water treatment

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Keywords: *silica aerogels, scaffold, polyurethane foams, thermal insulation, heavy metals adsorption.*

Nowadays, one of the challenges facing our society is producing advanced materials to deal with the current sustainability goals and energy regulations [1]. Among the candidates, aerogels are gaining increasing attention standing out for their unique properties. Their high porosity, huge surface areas, in combination with an excellent thermal insulation, among other properties, place them in the focus of numerous sectors such as automotive, building, or environmental.

Nevertheless, silica aerogels are usually reinforced in order to increase their mechanical strength by means of modifications in the precursors, cross-linking or fiber reinforcement [2]. Aiming to overcome some of the difficulties arising from these strategies an innovative approach has been developed in this work consisting on using the reticulated skeleton of polyurethane foams as scaffold during the synthesis of silica aerogels. The main advantages of this strategy are providing a homogeneous support and avoiding the common brittleness of these materials. The obtained composites presented super-insulation with values of the thermal conductivity between 12-14 mW/mK and a significantly improved mechanical stability [3]. Moreover, by modifying the silica formulation, these composites showed high adsorption capacities for removing heavy metals from water, improving the adsorption capacity of the monolithic aerogel by the appearance of strong synergies between both matrixes.

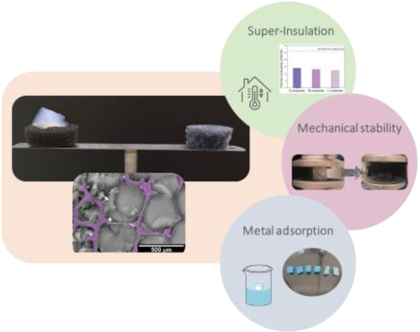

Figure 1 – Main properties obtained when reinforcing silica aerogels with reticulated polyurethane foams.

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Lignin based hydrogels for ionic thermoelectric applications

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Keywords: *Ionic thermoelectric materials, Lignin, Hydrogels, Sustainable.*
AMatS3.- Smart materials with advanced functionalities.

Since the recent discovery that some electrolytes can provide ionic Seebeck coefficients that are hundred times larger than the electronic Seebeck coefficient of "good" thermoelectric materials, ionic thermoelectric systems are considered to be a crucial breakthrough in the thermoelectric field that can allow production of highly efficient materials from abundant and sustainable sources. Thermoelectric applications are typically based on thermodiffusion of electronic charge carriers (electrons or holes) in semiconductors, semimetals, or metals due the Seebeck effect. However, in the case of ionic materials, the thermoelectric effect is induced by the thermodiffision of ions. During the last few years, ionic thermoelectric platforms have emerged as potential candidates for novel and high efficient thermoelectric materials [1]. This study explores the potential of lignin-based hydrogels as ionic thermoelectric platforms made from clean and sustainable resources. Thermoelectric properties such as the Seebeck coefficient, electrical conductivity, and thermal conductivity were studied to evaluate the performance of the hydrogels.

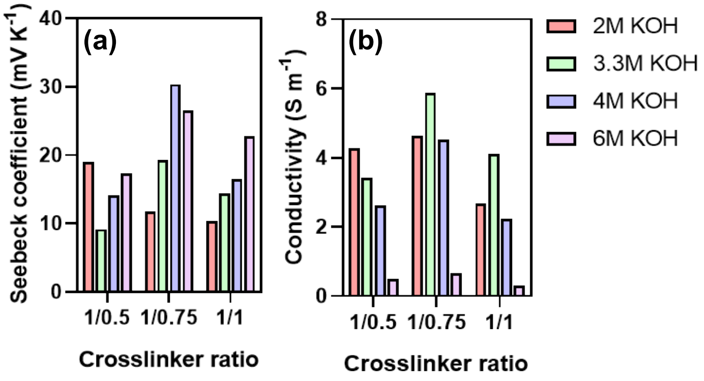

Figure 1 – (a) Seebeck coefficients and (b) Electrical conductivities as a function of KOH concentration and crosslinker ratio.

The conducted measurements revealed substantial Seebeck coefficients, varing from 9.17 to 30.42 mV K^{-1} (see Figure 1(a)). The electrical conductivity of the diferent samples showed relativetly good valueas spanning from 0.30 to 5. S m^{-1}(see Figure 1(b)). The thermal conductivity ranged from 0.19 to 0.4 W mK^{-1}.As a result, the power factor of the samples was calculated by combining the Seebeck coefficient and electrical conductivity measurements, yielding values as high as 4187 micro-watts per meter-Kelvin squared (μW m^{-1} K^{-2}). When combined with the thermal conductivity and absolute temperature, the materials achieved a thermoelectric Figure-of-merit as high as 3.53. These values, comparable to state-of-the-art materials in the field of ionic thermoelectric materials, highlights the remarkable potential of these lignin-based hydrogels as sustainable materials for energy.

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AMatS

2ND CONFERENCE ON
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NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

FOCUSED ION BEAM INDUCED DEPOSITION FOR OPTIMIZATION OF SUPERCONDUCTING TUNGSTEN-BASED DEPOSITS ON SCANNING PROBE MICROSCOPY CANTILEVERS

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Keywords: *FIB, FIBID, SQUID, superconductivity.*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Superconducting nanostructures exhibit unique properties and thus have many promising applications in the development of high-precision sensors [1]. The present work deals with the fabrication of tungsten-based nanoscale Superconductive Quantum Interference Devices (nanoSQUIDs) on Scanning Probe Microscopy (SPM) cantilever tips as part of the FET-OPEN project FIBSUPERPROBES (grant agreement 892427). The resulting SQUID on Tip (SOT) sensors would allow SPM to map magnetic fields, magnetic susceptibility and electric currents, giving researchers deeper insight into 2D materials. In the present work nanoSQUIDs are fabricated by means of Focused Electron/Ion Beam Deposition (FEBID/FIBID), direct write techniques that allow the growth of superconducting materials on different substrates independent of their topography.

Extensive research on tungsten-based nanostructures deposited by means of FIBID has been carried out. The resulting deposits generally exhibit superconducting behavior at temperatures below 4-5 K [2] and interesting properties such as vortex phenomena [3] and tunable T_c [4]. Tungsten-based SQUIDs presenting current modulation have also been successfully deposited on planar silicon substrates with 300 nm thermally grown silicon dioxide [5].

In this work, we optimize the growth conditions of tungsten deposits wires on silicon cantilevers with 50 nm thermally grown silicon dioxide by Ga^+ FIBID using $W(CO)_6$ as the precursor gas. Results show different growth rates in cantilevers and planar substrates. We have conducted experiments on chemical composition and growth rate under different deposition parameters to optimize the deposition process for future application in tungsten-based SOT fabrication.

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LA3 Electron jets in quantum graphene devices

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One-dimensional graphene devices are of great interest to study mesoscopic quantum transport phenomena. On one hand, one can define one dimensional channels by electrostatic gating with the advantage that the edges do not play a significant role in the transport characteristics. On the other hand, atomically precise graphene nanoribbons (GNRs) are predicted to exhibit exceptional edge-related properties, such as localized edge states, spin polarization, and half-metallicity. However, creating a good contact between electrodes and GNRs has been a longstanding challenge as it requires the controlled fabrication of sub-20 nm metallic gaps, a clean GNR transfer minimizing damage and organic contamination during the device fabrication, as well as work function matching to minimize the contact resistance. Here, I will discuss examples of both approaches: electron focusing and collimation experiments in bi-layer graphene channels defined by electrostatic gating and our progress in contacting 9-atom-wide armchair-edged GNRs with Pt, MoRe and Pd contacts.

CURCUMINOIDS AS MOLECULAR PLATFORMS FOR RESPONSIVE AND CONDUCTIVE MATERIALS

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Keywords: *molecular platforms, curcuminoids, responsive materials, surfaces, curcuminoids*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Molecular and supramolecular nanomaterials and active surfaces are one of the fields that have attracted intensive research due to their potential applications in different fields such as development of sensors or multicomponent systems. In this sense, knowing the great chemical versatility of Curcuminoids (CCMoids), which are derivatives of curcumin, their conjugated nature, their fluorescent behavior and the possibility of coordinating both metals and metalloids, and given that such coordination affects their electronic/fluorescent performance [2], we are interested in the preparation responsive materials based on CCMoids as molecular platforms. Indeed, we here present how we are exploring the preparation and using CCMoids-based monolayers towards the development of metal detectors and in molecular electronics by building electrode-CCMoids-electrode junctions. On one hand, new fluorescent CCMoids with pyrene groups are immobilized covalently on glass and Si-based surfaces. Therefore, the change in the fluorescence of the surfaces depending on the metal or metalloid coordinated and the possibility of the metal released upon coordination have been studied, Figure 1A. On the other hand, we have synthesized CCMoids functionalized with ferrocenes (Fc) that have double function (Figure 1B): surface anchor groups thought the formation of supramolecular complex with cucurbit[7]uril (CB[7]) monolayers and as head groups to generate CCMoids-based junctions and study their conductivity [3]. Therefore, the formation of active CCMoids-surfaces by covalently or supramolecular immobilization of CCMoids will be presented as well as their functionality for the development of multifunctional materials.

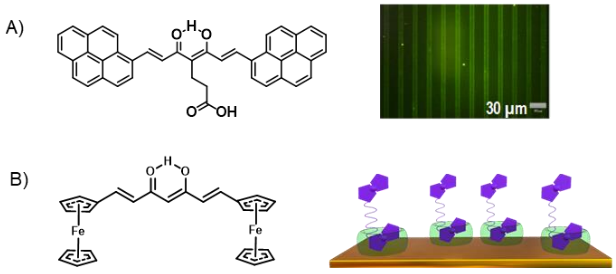

Figure 1 – A) Chemical structure of fluorescent CCMoid and its corresponding fluorescent patterned monolayers; B) Chemical structure of ferrocene functionalized CCMoid and their immobilization on CB[7] monolayers

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Is the surface of Hofmann-like spin-crossover {Fe(pz)[Pt(CN)4]} the same as its bulk?

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Keywords: *Magnetic properties, XPS, Spin transition.*

Indicate one of the following areas: AMatS3.- Smart materials with advanced functionalities.

Temperature dependent X-ray photoemission spectroscopy (XPS) has been employed to examine the spin-crossover (SCO) transition in the nanocrystals of the 3D Hoffman-like {Fe(pz)[Pt(CN)4]}. In consistence with the existing literature, the temperature-dependent variations in the Fe 2p core-level spectrum provide unambiguous evidence of the spin-state transition in this SCO complex [1, 2]. A lack of discernible temperature-driven shifts in the binding energies of both the N 1s core-level components indicates that the HS electronic configuration of this complex is somewhat immune to thermal fluctuations. The high-spin fraction versus temperature plot, extrapolated from the XPS measurements, reveals that the surface of the nanocrystals of {Fe(pz)[Pt(CN)4]} is in the high-spin state at room temperature, rendering it promising for room-temperature spintronics and quantum information science applications [3].

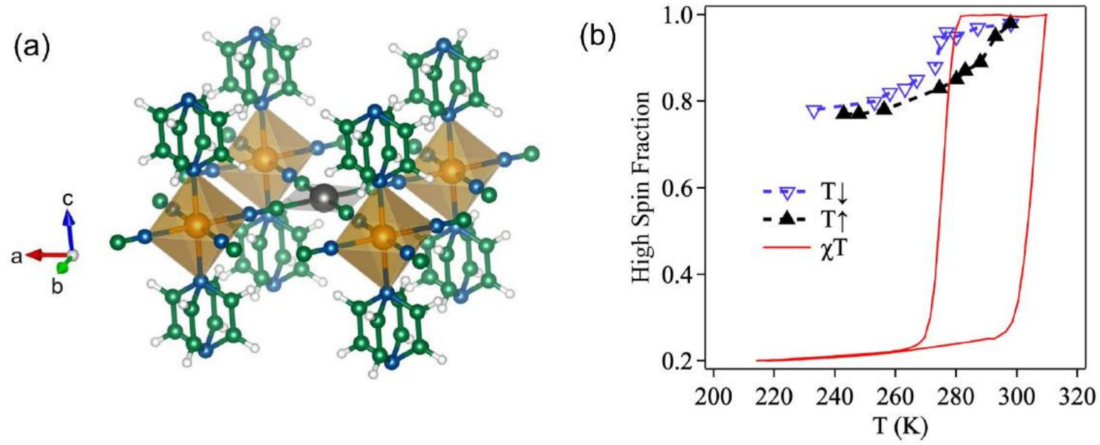

Figure 1. (a) Ball-and-stick model of the 3D Hofmann-like spin-crossover porous coordination polymer {Fe(pz)[Pt(CN)4]}, where pz = pyrazine. Atom codes: Fe (orange); N (blue); C (green); Pt (gray); H (white); (b) Normalized high-spin fraction of {Fe(pz)[Pt(CN)4]}, extrapolated from XPS (solid black and hollow blue triangles) and magnetic susceptibility measurements (red curve), as a function of temperature.

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CRYO FOCUSED ION BEAM INDUCED DEPOSITION: ULTRAFAST GROWTH OF FUNCTIONAL MATERIALS AT LOW TEMPERATURES

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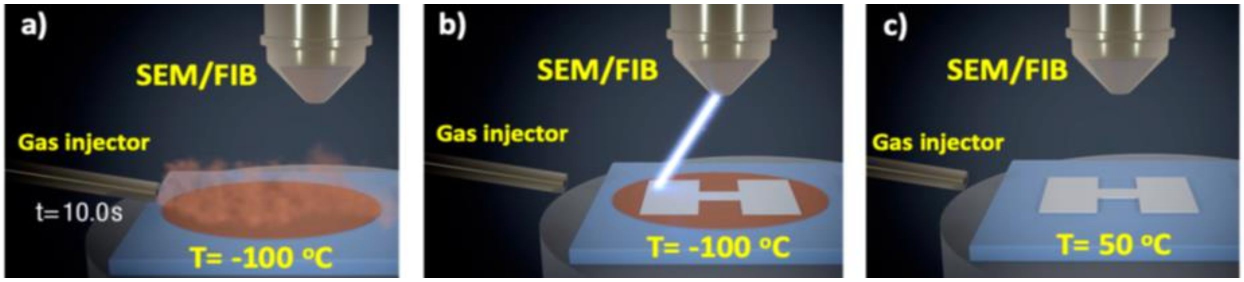
Keywords: *focused ion beam induced deposition; electrical contacts; cryogenic conditions; metal layers.*

Cryo Focused Ion Beam Induced Deposition (cryo-FIBID) is an advanced nanofabrication technique that operates at low temperatures (i.e. -100°C) to increase several orders of magnitude the deposition rate with respect to room-temperature (RT) FIBID [1]. In this approach, when the precursor gas is injected, a condensed precursor layer is formed on the substrate due to the strongly reduced diffusion rate of the precursor molecules adsorbed at low temperature (see Figure). Then the condensate is ion-beam irradiated to produce the decomposition of the molecules, resulting in an accelerated growth at lower doses or reduced exposure time, as well as minimizing side effects such as ion implantation, amorphization and milling. When the sample is heated up to RT, the unexposed condensed precursor evaporates, and the irradiated pattern remains as the final deposited structure.

Cryo-FIBID has allowed the growth of W-C [2], Pt-C [3], and Co [4] nanostructures with liquid nitrogen as a cooling agent (-100ºC), as well as W-C using a thermoelectric plate (-60°C) [5]. It also provides deposits with high metal content and low resistivity. We present here our recent advancements on cobalt deposits grown by cryo-FIBID in terms of substrate compatibility. The substrates tested were Si, SiO_2, Au, Al, graphene, $LaAlO_3$ and $SrTiO_3$, using different irradiation doses of 5-55 $\mu C/cm^{-2}$. We also analyzed the resolution limit of cryo-FIBID Co-based deposits, and we found that thin lines of up to 20 nm thickness and width can be deposited. These results open up the possibilities for the use of cryo-FIBID Co deposition for different applications, such as circuit editing, electrical contacts, and mask repair.



Schematic illustration of the cryo-FIBID process.

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Ultrathin ferroelectric HfO_2 epitaxial films

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Keywords: ferroelectrics, oxides, HfO_2, epitaxy, thin films

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Ferroelectric HfO_2, a CMOS compatible material, holds great promise for new memory and energy devices [1]. It is necessary to advance in the understanding of the mechanism of ferroelectricity and improve some properties. Ferroelectric HfO_2 research has mainly focused on polycrystalline films. Epitaxial films are currently being investigated and are of great interest to understand the properties and prototyping devices [2]. Ferroelectric hafnia can be epitaxially stabilized on oxide single crystals or on buffered Si(001) wafers. The ferroelectric orthorhombic phase is metastable and usually coexists with paraelectric phases. Control of polymorphs is critical to maximize ferroelectric polarization. Here, I will show that phases can be effectively controlled by epitaxial stress engineering [3]. I will also show that ferroelectric films of doped HfO_2, even with a thickness of less than 5 nm, can present a high polarization greater than 20 $\mu C/cm^2$, endurance of more than 10^{11} cycles, and retention longer than 10 years, overcoming the dilemma existing between these properties. These results are achieved in films integrated with Si(001) [4].

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POSTERS – LA3

ANALYSIS OF THE STRUCTURE, FUNCTION, AND USE OF PLASTICIZERS AND PVC MEMBRANES IN POTENTIOMETRIC SENSORS

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Keywords: *Polyvinyl chloride, potentiometric sensors,plasticizers, polymeric membranes*

AMatS3.- Smart materials with advanced functionalities.

Polyvinyl chloride (PVC) is a synthetic plastic polymer used in the development of potentiometric sensors. Properties such as chemical resistance, electrical insulation, biocompatibility, low cost etc define this polymer as excellent material to create polymeric membranes. Sensors based on this polymer, are able to measure a high range of compounds, which means, these sensors can be implicated in several fields [1].

In this occasion, potentiometric sensors based on PVC membranes have been developed for the evaluation of the electric current and the quantification of analytes that are presents in different food and beverages, such as tartaric and lactic acids. These membranes have to include specific characteristics to allow their selectivity, permeability to ions, durability and compatibility with the sample. For that reason, the correct combination of the compounds that performs the membrane is crucial to respond to specific classes of ions or chemical compounds, for that the inclusion of adequate ionophore agents normally results essential [2,3].

This work is based on the study of the influence of the type and percentage of PVC used in the membranes development (high- and low-density PVC) and the type and percentage of plasticizers (two types have been selected based on their ramifications). The presence of the plasticizer favors better performance and versatility in the use of the sensors due to it increase the flexibility of PVC. Moreover, the plasticizer can play an important role in chemical stability and greater electrical efficiency, as it modifies the technical characteristics, improving also the sensitivity and durability.

The main purpose of this work is to found the best percentage combination of plasticizer and PVC, as well as the type of both of them to be used in the preparation of membranes to provide the best performance. It has been concluded that the relationship between plasticizer and PVC in the preparation of polymeric membranes is essential in the response of potentiometric sensors.

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BIOPOLYAMIDE COMPOSITES FOR FUSED FILAMENT FABRICATION: GLASS FIBRE AND NANOCLAY

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Keywords: *Fused Filament Fabrication, Biopolyamide, Fibre Reinforced Polymer, Nanocomposites, Thermo-mechanical properties.*

AMatS3.- Smart materials with advanced functionalities

Additive manufacturing provides new opportunities for the mass customization of parts, decreased energy consumption, and improved materials utilization. Among the different 3D printing technologies fused filament fabrication (FFF), which relies on the extrusion of a thermos plastic filament melt through a nozzle and the selective deposition on a surface to build up apart in a layer-by-layer manner, is the most used. The most common polymers used for this technology are ABS and PLA, but both have mechanical and temperature limitations for engineering applications. In recent years, other materials such as PC, PEEK or PEI have been used, which present good thermo-mechanical properties, but also processing difficulties that require the use of more complex and high-cost printers. Polyamides have been extensively examined for 3D printing by selective laser sintering (SLS), with polyamide-12 being the most common polymer. However, for FFF there are only a few grades of polyamide-6, which are specially designed to be processed in professional tools to prevent the deformation of the final parts due to the high crystallinity and the trend to water-absorption of these materials. In this work different fibre composites based on biopolyamide-11 were prepared by melt extrusion, converted into filament, printed by FFF, and characterized [1]. The addition of both glass fibre and fibrillar nanoclay improve dimensional accuracy of the final part, allowing the processing of these materials in conventional printers [2]. Focused on thermo-mechanical properties, the difference between the composites were systematically examined as a function of fibre type, amount and printing orientation, accompanied by an in-depth analysis of the internal morphology of the parts by X-ray MicroCT to establish the different reinforcement mechanisms (Figure 1).

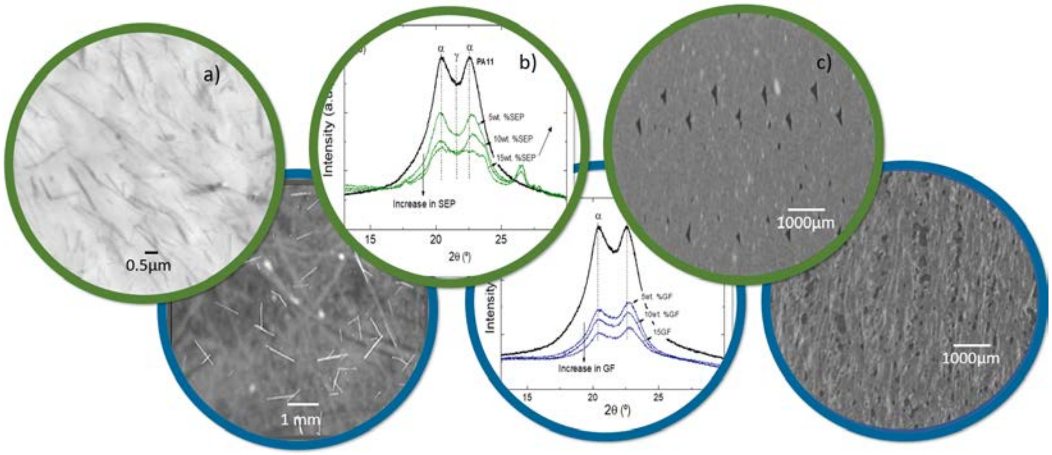

Figure 1. (a) TEM (b) WAXS and (c) MicroCT for nanocomposite (green) and glass fibre composites (blue).

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CARBON DOTS AS PHOTOACTIVE SENSITIZERS

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ABSTRACT

Carbon nanodots (CNDs) have emerged as novel fluorescent nanosensitizers that combine a series of appealing properties such as: (i) high colloidal stability in water and physiological media; (ii) high photo-stability and resistance to photobleaching; (iii) reduced toxicity in comparison with nanosystems containing heavy and potentially toxic elements; (iv) tunable optical response spanning from UV to NIR ranges including large two-photon excitation cross-sections; (v) abundance of inexpensive raw precursors for their synthesis. We propose the use of laser pyrolysis to tune the synthesis of carbon nanodots as active by modifying the starting organic precursor and taking into account the presence of N doping species.We describe the use of CNDs retrieved by laser pyrolysis, their deposition onto P25 and their application as NIR-active photocatalysts to consume glucose and generate Reactive Oxidative Species (ROS). These hybrids can be successfully used for photodynamic therapy (PDT) against cancer cells under NIR irradiation.

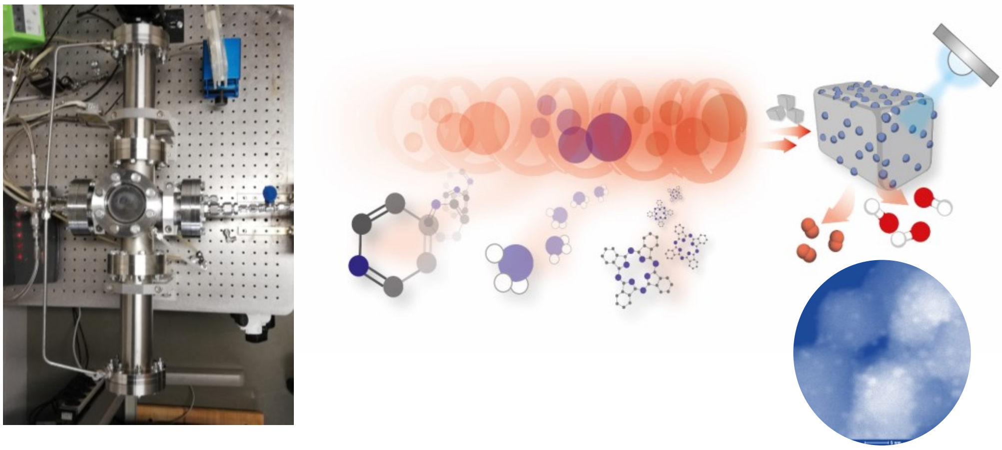

Figure: *Left panel: Reactor for laser pyrolysis of carbond dots; Right panel: schematic representation of different precursors used to obtain carbon dots and their subsequent deployment on P25 nanoparticles.*

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CERAMIC SCAFFOLDS OBTAINED THROUGH CERAMIC STEREOLITHOGRAPHY WITH POTENTIAL APPLICATION IN BONE TISSUE REGENERATION.

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Keywords: *Scaffolds, stereolithography, TPMS, Alumina.*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: NO

Scaffolds are structures that mimic the characteristics of the extracellular matrix of affected organs or tissues and facilitate the interaction of implantable devices used in the process of bone repair or regeneration. They must have high porosity, with well distributed and interconnected pores to facilitate cell penetration, nutrient diffusion, and vascular growth. In addition, coexistence between the material and the new tissue must be allowed without affecting the biological environment [1], so biomechanical properties must be compatible with the native tissue, making it necessary to achieve an optimal balance between porosity and mechanical strength for new bone tissue formation [2]. Triple-periodic minimal surfaces (TPMS) possess geometries that are outlined as suitable for use as scaffolds. Stereolithography 3D printing and digital light processing (DLP) are techniques that facilitate the production of ceramic bodies with TPMS-type geometries, offering advantages such as greater precision and efficiency compared to other additive manufacturing techniques. Different authors have addressed the issue of alumina-based scaffolds, demonstrating that with this material high quality parts can be obtained, with good mechanical properties thanks to the microstructures obtained [3–5]. In general, the use of alumina has increased significantly in medical fields as an alternative to replace metal parts in bone components such as femoral or dental due to its good mechanical properties, anticorrosion and chemical stability, which prevents it from dissolving in the physiological environment. However, there are no precedents of studies where all-alumina ceramic scaffolds with TPMS-type geometries are developed through the ceramic stereolithography technique. In the present work, a light-curing resin mixture with different percentages of alumina particles is developed to be implemented in the printing of ceramic scaffolds with gyroid and primitive TPMS geometry by the ceramic stereolithography technique for possible biomedical applications. The resin was characterized, and the rheological behavior of the different suspensions was studied to verify that the rheological conditions favored the printing of the parts. Scaffolds of the composite with gyroid geometry were obtained, which underwent a controlled heat treatment to eliminate the resin and sinter the ceramic bodies. The resulting ceramic scaffolds were characterized morphologically and mechanically. The study is still in progress, and it is planned to continue with their respective biological analyses.

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Controlling magnetism by applying an electric field

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Keywords: *Magnetoelectronics, magnetoelasticity, magnetic alloy, magnetic anisotropy*

AMatS3.- Smart materials with advanced functionalities.

Internet of Things and Artificial intelligence/Machine learning are growing exponentially, and the total energy consumption in all microelectronics could add up to a significant part of primary energy by 2030. Large decrements in energy consumption, by several orders of magnitude, demand incorporating new concepts in the design of these components. One of them is using electric fields to control magnetism instead of an electric current to generate magnetic fields or polarized spin currents. Magnetoelectric (ME) heterostructured materials with strain-induced coupling between ferroelectric and magnetostrictive components provide the larger converse ME coupling for low-energy consumption applications [1]. In this contribution, we present magnetic and ME properties of crystalline FeGa films grown on MgO and ferroelectric PMN-PT crystals. FeGa alloys around the galfenol composition are attractive because of their large magnetoelastic coupling with low magnetic anisotropy values, which tend to conceal strain-induced effects. Crystalline FeGa films with on the (001) orientation display one the highest values of the converse ME coefficient, above 10^{-5} s/m [2], with the easy direction switching between in-plane [100] and [010] directions by the application of an external electric field which activates an uniaxial anisotropy. Direct measurement of the magnetoelastic stress in films grown on MgO(001) indicates that both irreducible coefficients exhibit bulk-like behavior.

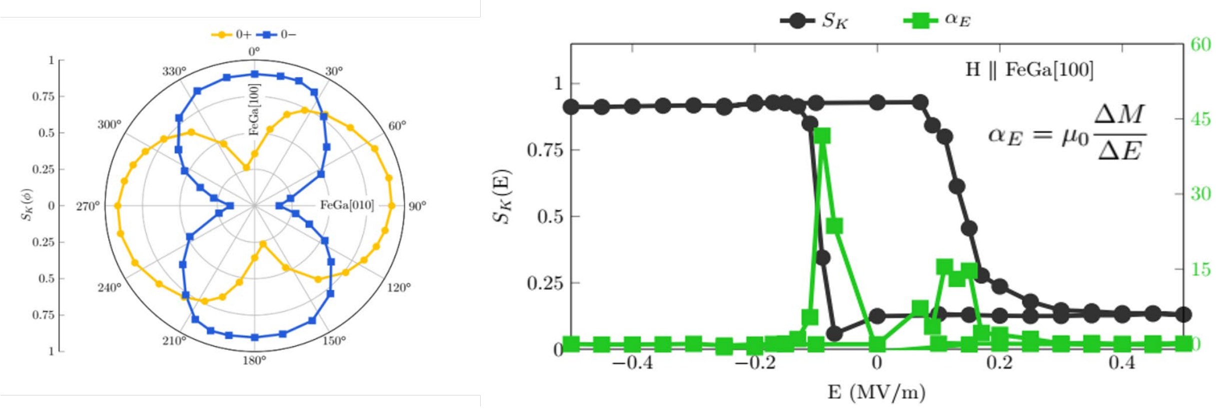

Figure: (Left) Squareness $_K$ as a function of the angle after applying a positive (0+) and negative (0-) pulse of electric field and (Right) S_K and α_E, the converse ME coefficient as a function of the applied electric field.

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Controlled fabrication of Nb-based dayem bridge Josephson Junctions for highly-replicable SQUIDs

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Superconducting quantum interference devices (SQUIDs) combine the physical phenomena of flux quantization and Josephson tunneling, resulting in a device that is extremely sensitive to magnetic field fluctuations. Due to their quantum behavior, SQUIDs are fundamental elements in the development of new quantum technologies in the field of sensing and computing.

They have the ability to perform broad frequency bandwidth ultrasensitive magnetic flux measurements at low temperatures. Therefore, they are commonly found in instruments such as amplifiers, magnetometers or gradiometers used in quantum sensing applications [1]. They area also suitable as tunable couplers, controlling the coupling between several elements, such as qubit-qubit interactions or qubit-quantum bus interactions thanks to their variable inductance characteristic [2].

To achieve high reproducible devices, a tight control over the fabrication process of the Josephson Junctions (JJ) -as the main constituents of SQUIDs- is required. To that end, we propose the fabrication of Nb-based nanobridge Josephson Junctions. The target area is protected by a Pt layer grown by focused-electron-beam-induced-deposition (FEBID) and Focused Ion Beam (FIB). Higher control is achieved in the fabrication process attaining a better reproducibility rate.

Figures

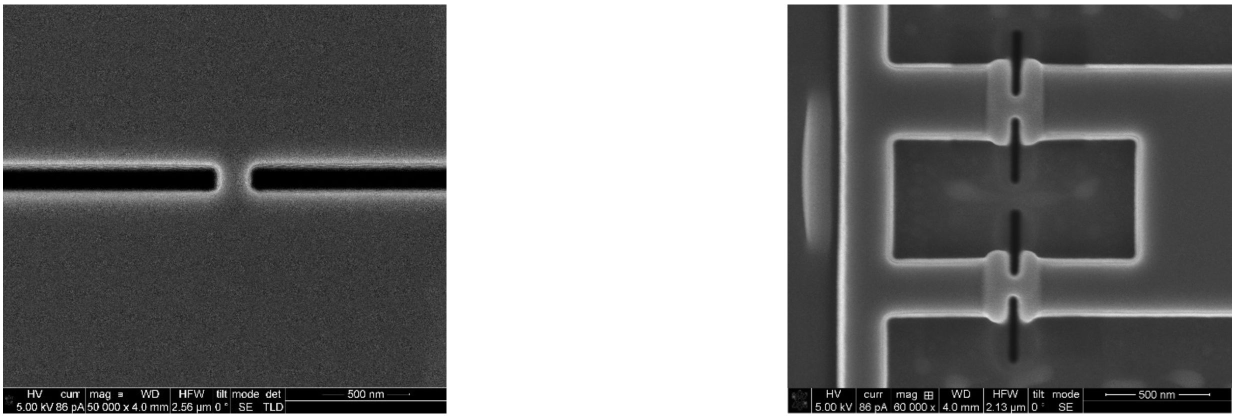

Figure 1: Caption of a nanobridge Junction (left) and a SQUID (right) with Pt deposited.

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2ND CONFERENCE ON
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ENHANCING HYDROLYTIC RESILIENCE: ORGANOCATALYSTS IN SINGLE-COMPONENT SMART POLYURETHANE ADHESIVES FOR DECORATIVE INSULATION FACADES

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Keywords: *siliciclastic sandstone; single-component polyurethane adhesive; metal-free catalyst; colorimetry; RGB parameters; homemade stability measurement system; DBU; naphthoic acid; fan; facades.* AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Our focus was on improving the thermal and hydrolytic stability of polyurethane (PU) adhesives, essential for industrial productivity [1,2]. We developed PU prepolymers designed to withstand varying ambient temperatures. These prepolymers combined traditional isocyanate-terminated PU with metal-free acid:base organic catalysts, where the choice of organocatalyst played a pivotal role in adhesive stability [3]. We assessed eleven latent organocatalysts produced from the reaction between 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and various acids. One catalyst, originating from 1-naphthoic acid, demonstrated exceptional stability, maintaining its integrity for at least three hours at 60°C and 65% relative humidity under rigorous stirring. We evaluated this stability using a fan-based stirrer and conducted kinetic analyses of curing conditions through differential scanning calorimetry (DSC). Furthermore, our adhesive formulation prioritized environmental sustainability by eliminating metals, particularly tin found in catalysts like dibutyltin dilaurate. To validate the practical utility of our adhesives, we conducted tests using decorative facade models composed of siliciclastic sandstone from Vilviestre del Pinar (Burgos, Spain) and extruded polystyrene (XPS). The results showcased outstanding hydrolytic and thermal stability, highlighting their potential for panel manufacturing [4].

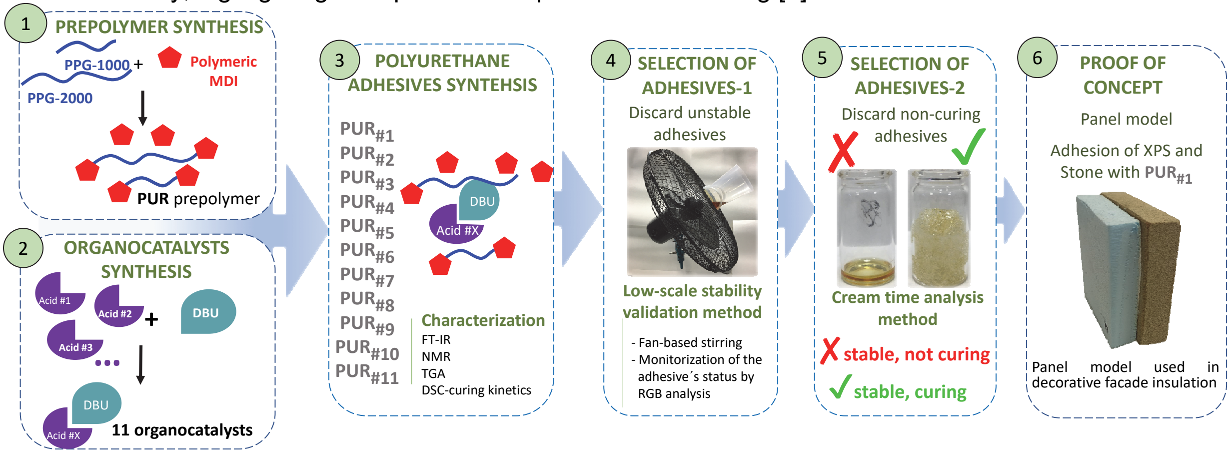

Figure 1. Table of contents.

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ENCAPSULATION OF COSMETIC ADDITIVES IN THERMORESISTANT MATERIALS FOR DEVELOPMENT OF FUNCTIONAL TEXTILE FIBERS

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Keywords: *Encapsulation, green synthesis, MOF, functional textiles*

Market competitiveness in textile industry makes necessary the development of new materials with high added value. Microencapsulation allows the preparation of fibers with different properties thanks to the incorporation of additives and allowing their controlled release, creating fabrics with added functionality. The encapsulation process is a useful strategy to increase thermal and chemical stability of the encapsulated compounds. Traditionally, the incorporation of capsules to the fibers has performed in the last phase and superficially, therefore their durability is quite limited and withstanding few washing cycles. In this work, the developed microcapsules, carried out in cooperation with Nurel S.A. company, are incorporated in the spinning process, so they are located inside the fibers improving their durability and resistance. For this reason, the microcapsules have to resist the high temperatures used in the industrial process. As encapsulating agents are studied three types of materials zeolite Y, a biopolymer and a metal-organic framework (MOF).

The procedure to encapsulate additives in zeolite Y and MOF obtaining special fibers has been developed elsewhere [1-2]. The biopolymer microcapsules are obtained using an emulsion crosslinking method. MOF synthesis has been performed through greener processes avoiding the use of solvents harmful to the environment and human health, such as dimethylformamide (DMF).

To compare the microcapsules, various fiber-processing conditions have been studied. The materials have been characterized using diverse techniques, such as, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), infrared spectroscopy (FTIR), high performance liquid chromatography (HPLC), ultraviolet-visible spectroscopy (UV-Vis) and gas chromatography-mass spectrometry (GC-MS).

In order to determine qualitatively and quantitatively the presence of the additive as well as its resistance under the high temperatures and other conditions of the industrial manufacturing process, the microcapsules and fibers are analyzed by TGA and FTIR. In addition to the above, solid-liquid extractions of the capsules and fibers are performed using various solvents and extraction conditions. The liquids obtained from these extractions are analyzed using HPLC, UV-Vis and GC-MS. Besides, SEM images were taken in order to check the correct distribution of the microcapsules inside the fibers and their resistance after the spinning process.

The results obtained show that with the polymeric capsules a greater quantity of encapsulated additive can be obtained but their resistance is compromised during the manufacturing process. The polymeric microcapsules have a limited thermal resistance while the ones of zeolite Y and MOF present a greater thermal resistance and both are able to withstand extrusion conditions.

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Engineering remote spin-spin interactions by superconducting circuit design.

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In spite of the staggering progress achieved in recent years [1], the computational volume of available quantum processors still limits their application to problems of socio-economical interest. Hybrid platforms, combining superconducting circuits and microscopic qubits, such as spins, provide additional opportunities to achieve a higher degree of integration. In particular, schemes based on molecular spins allow scaling up quantum resources within each unit, via chemical design of molecules behaving as multiple qubits or qudits, and via the proper engineering of the superconducting circuit [2,3]. Here, we address this second option.

We focus on circuits based on lumped element LC resonators. Compared to coplanar resonators, often used to read out superconducting qubits, they offer a higher design flexibility. The relevant resonator properties, i.e. the resonance frequency ω_r and quality factor Q, can be widely tuned without affecting the transmission through the readout line. Besides, many resonators can be coupled to the same transmission line, which allows multiplexing the readout. Here, we exploit these properties to design and realize resonator pairs able to introduce communication channels between remote spin qubit ensembles (Fig. 1).

A superconducting chip consisting of seven couples of LC resonators has been designed and fabricated. All resonators have a different ω_r, ranging from 2 GHz to 3.5 GHz, which makes them individually addressable. Couplings between resonators, different in each pair, have been engineered by the design of the two capacitors and their mutual distances. We have simulated the microwave transmission through the readout line and shown that it bears evidences for the effective coupling, mediated by the circuit, between spin qubits placed onto each of the two inductors. Furthermore, the effective spin Hamiltonian of this hybrid system can be obtained, and its parameters tuned, in terms of controllable variables such as the inductance and capacitance of each LC resonator. Potential applications for the implementation of universal quantum gates and/or the storage of quantum states in a quantum memory are analyzed on basis of this model using real parameters.

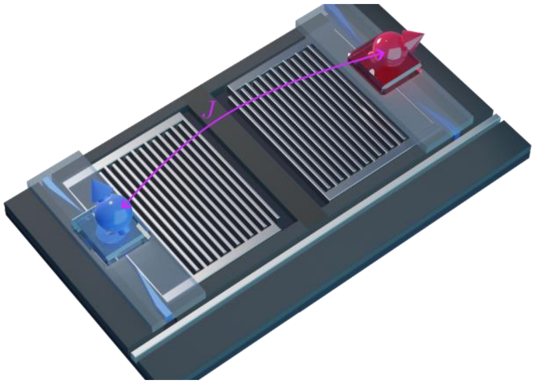

Fig. 1: Communication between remote spin qubit ensembles positioned on a pair of LC coupled resonators.

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EVALUATION OF PROTEIN CORONA IN BONE REGENERATION

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Keywords: *mesoporous bioactive glasses, protein corona, drug delivery, osteogenic properties*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Mesoporous bioactive nanoparticles with composition SiO2-CaO (NPs-Ca) have gained attention in the past few years. The main reason of its interest is their high porosity, robustness and great loading capability [1]. In addition, they showed high bioactivity, biocompatibility and promoted bone formation in vivo [2]. Moreover, protein corona has been evaluated in several nanomaterials, however its influence in the osteogenic activity has not been widely studied.

On the other hand, among the different molecules with osteogenic properties, simvastatin (SIM) has demonstrated high efficiency, specially combined with biomaterials [3]. However, this approach does not explore SIM in combination with highly porous materials. Therefore, the combination of NPs-Ca and SIM seems to be a simple, but effective strategy to enhance cell differentiation into osteoblast phenotype, thus promote bone regeneration. In this context, the use of NPs-Ca as local drug delivery systems combined with SIM provide promising strategies for the reconstruction and treatment of bone defects.

In this work, we have evaluated the effect of calcium in the protein corona by synthetizes NPs-Ca with different amounts of calcium, as well as the effect of protein corona formation in cell proliferation and differentiation. In addition, we loaded SIM in NPs-Ca to evaluate the synergy between Ca and SIM in terms of osteogenic capacity. In vitro studies with mice preosteoblast MC3T3-E1 showed an increase in alkaline phosphatase activity and mineralization. According to these results, the osteogenic properties of NPS-CA-SIM presents potential to be used as implants for biomedical applications, being the first step to create more complex systems.

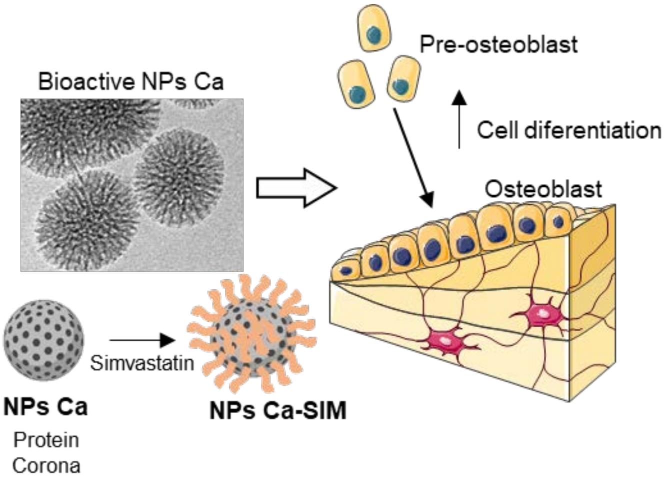

Figure 1-TEM image of NPs-Ca and scheme of the effect of NPs-Ca-SIM to enhance MC3T3-E1 pre-osteoblast differentiation to osteoblast phenotype.

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GROWTH AND CHARACTERIZATION OF NOVEL IR1–XCOXO2 THIN FILMS

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Keywords: *iridates, spintronics, XAS*

AMatS3.- Smart materials with advanced functionalities. (TICs)

Poster contribution. Interested in participating in the Poster Flash/Elevator Pitch session: NO

IrO_2 is one of the most promising materials for the development of new SOT-MRAM magnetic memories. In particular, IrO_2 is a very suitable material for spin–current detection due to the high spin–orbit coupling (SOC) of the Ir ions that makes possible an efficient conversion of pure spin-currents on charge-currents via the so-called inverse spin Hall effect (ISHE) [1, 2]. In order to further improve its spin–current detection performance doping with different elements appears as a natural route. Among other effects, the different ionic size of the dopant may give rise to contraction/elongation of the lattice and/or distortions that can significantly change the electronic structure. Similarly, the dopant ions can induce relevant changes in the oxidation state of the host. The doping of IrO_2 with 4+ ions, such as Sn^{4+} and Cr^{4+}, has been reported to give rise to strong changes in its electronic and/or magnetic behavior [3,4]. On the other hand, the effect of increasing the oxidation state of Ir in IrO_2 films has remained unexplored to date, even when in other iridium oxide series, a larger SOC has been reported for Ir^{5+} relative to Ir^{4+} [5]. Here, $Ir_{1-x}Co_xO_2$ thin films have been prepared by reactive magnetron co–sputtering deposition. Composition, structure, oxidation state and magnetic behavior have been analyzed. After annealing, an $Ir_{1-x}Co_xO_2$ substitutional solid solution phase was achieved for a wide Co-doping range ($0 \leq x \leq 0.5$). The rutile crystal structure was found to contract with increasing Co content. XAS spectra show that the oxidation state of cobalt is Co^{3+} and that this triggers an increase in the oxidation state of Ir, up to ~ 5+ in the $Ir_{1-x}Co_xO_2$ samples with higher Co content. By application of sum rules, a 13% increase in the SOC is found despite the lattice shrinkage causing a detrimental bandwidth broadening. In addition, our work shows that the magnetic response of the doped films remains paramagnetic with no enhancement of the susceptibility, thus indicating a non-magnetic low spin Co^{3+} electronic configuration, and a slight increase (a factor 5 for 40% doping) of the electronic resistivity. These results clearly indicate a route for further optimization of the performance of the IrO_2 as spin current detectors.

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HOW SILVER NANOWIRES CAN IMPROVE THE PERFORMANCE OF ELECTROCHEMICAL BIOSENSORS

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Keywords: *silver nanowires, biosensor*

Area: AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Nanomaterials are taking an essential role as sensing materials in electrochemical sensors. Metallic nanoparticles have been extensively used as the sensing layer of such sensors due to their high surface to volume ratio and their excellent electrocatalytic porperties [1]. Metallic nanowires are an interesting option to obtain effective sensing layers owing to their high aspect ratio that can enhance the contact surface between the sensing layer an the analyte with respect to the nanoparticle analogues[2]. In this work, silver nanowires (AgNWs) films have been exploited to design electrochemical sensors and biosensors for the detection of a variety of compounds of interest in the food industry (phenols and sugars among others). AgNWs films have been obtained by spin coating or drop casting methods and AFM studies have demonstrated the homogeneous distribution of AgNWs on the electrode surface. Substrates covered with AgNWs show improved responses towards catechol or sugars with higher sensitivity and lower limits of detection (LOD). In addition, AgNWs can be used as electron mediators in biosensors. In our studies, AgNWs have been covered with a variety of enzymes including tyrosinase (for the detection of phenols) and galactose oxidase (to detect lactose and galactose). AFM images show a homogeneous distribution of the enzymes along the silver nanowires, maximizing the contact surface (Figure 1). The large contact area promotes the electron transfer between the enzyme and the electrode surface, resulting in LOD in the range of 10^{-6} M, which is one order of magnitude lower than the LOD obtained using an AgNPs. The calculated Michaelis-Menten constants were, two orders of magnitude lower than reported in similar biosensors using metallic nanoparticles. These results make AgNWs promising elements in nanowired biosensors for the sensitive, stable and rapid voltammetric detection of phenols in real applications.

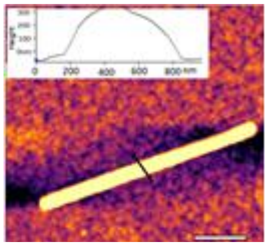

Figure 1 – AFM of the AgNW covered by Tyrosinase

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Magnetostatic spin waves in shaped ferromagnets

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When a magnetic metal is placed on top of a superconducting transmission line, such that the generated magnetic field affects the metal, its spins start preceding, causing **spin waves**. Under different values of the generated magnetic field, these **spin waves** cause resonance within the material. These resonances are called magnetostatic modes, being the Kittle mode the fundamental of these resonances.

In this work we study from the theoretical point of view the mathematical formulation of the Kittle modes, both from the fundamental mode [1] and the first excited modes[2]. Then we fit these theoretical formulas with the observed experimental results for different magnetic thin films with different aspect ratios and applied magnetic fields in their different axes.

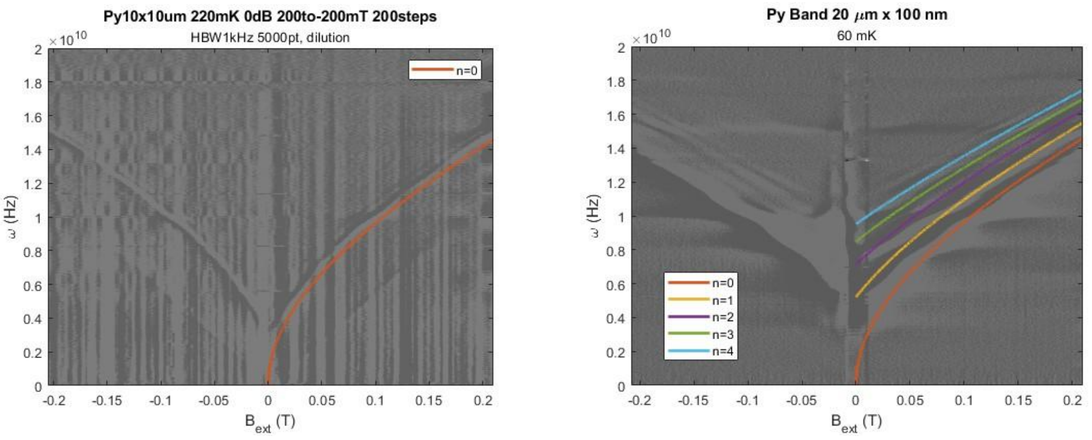

Figura 1. Theoretical plots on the experimental result for the resonance frequencies in function of the magnetic field. In the left picture we can observe a curved white line, vertically symmetric with respect to B_{ext} =0 T, with a red curve, being the theoretical plot. In the right picture, the first 4 modes, along with the fundamental one can be observed, both from the experimental result and the theoretical plots.

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METAL-ORGANIC FRAMEWORKS IN SUSTAINABLE 3D-PRINTED DEVICES FOR ORGANIC CONTAMINANTS EXTRACTION

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Keywords: *Metal-organic frameworks, 3D printing, fused deposition modelling, pollutant extraction, remediation*

Indicate one of the following areas:

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Metal-organic frameworks (MOFs) are a type of crystalline material that possesses many fascinating characteristics, such as a large specific surface area, high porosity, uniform and adjustable pore size, and tunable functionality. These features make them interesting candidates in several areas, including gas storage, (photo)catalysis, drug delivery, and electrochemical applications, among others. In recent years, due to these excellent properties, MOFs have also been efficiently used for the adsorptive extraction and removal of pollutants [1, 2]. An important and critical step during the extraction process of contaminants using MOF-based materials, especially when using powdered solids, is the laborious and often incomplete recovery of the adsorbent. On the other hand, most of them exhibit rigidity and are challenging to mold due to their powdered nature, which imposes restrictions on their practical applications. Consequently, it is highly desirable to develop strategies to create composites and processing methods to consolidate MOFs into a monolithic material. To this end, additive manufacturing (3D printing) has attracted considerable attention in several fields due to its attractive advantages, such as easy handling, the ability to manufacture complex shapes, and customized designs at a low cost. In fact, the development of novel functional 3D printed devices for pollutant extraction [3, 4] has been addressed (mostly aimed at dye removal) in recent years. However, the sustainability of these devices, both in terms of MOF synthesis and 3D printing materials, is not usually considered. In this communication, we present the development of MOFs incorporated into environmentally sustainable 3D-printed structures designed to capture organic pollutants, specifically antibiotics and herbicides, from water bodies. To achieve this, we designed and developed 3D-printed devices using fused deposition modeling (FDM) as 3D printing technique and sustainable filaments. Subsequently, we optimized the post-printing solvothermal growth of MOFs on the external surfaces of these 3D-printed structures and we proceeded to their characterization. The obtained functional devices were tested for the extraction of organic pollutants.

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Acknowledgements

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Optimizing the protein corona of PEI-coated mesoporous silica nanoparticles for efficient gene transfection

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Keywords: protein corona, gene transfection, mesoporous silica nanoparticles, immune response, drug delivery

Indicate one of the following areas:

AMatS1.- Graphene and other 2D materials.

AMatS2.- Materials for Energy.

AMatS3.- **Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)**

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES/**NO**

In the last few years, the vehiculization of nucleic acids to modulate certain responses in the organism has attracted the attention of many researchers. Those nucleic acids are negatively charged and, consequently, adsorbing them onto a cationic surface might be a good strategy to administer them to the organism. In this regard, polyethyleneimine (PEI) has long been employed to coat nanoparticles to render positive surface charges. Nonetheless, it is well known that PEI may induce toxicity depending on the dose, molecular weight of conformation [1]. In addition, highly cationic surfaces are known to trigger the formation of a thicker protein corona, which may lead to nanoparticle recognition by the immune system [2]. To address such drawbacks, poly(ethylene glycol) (PEG) constitute a biocompatible polymer that may be employed to improve the cyto and biocompatibility of these nanocarriers.

In this work, we have synthesized and characterized a series of PEG/PEI-coated mesoporous silica nanoparticles for application in gene transfection. In this regard, different polymeric blends have been conjugated to the nanoparticles and characterized, looking for different protein corona profiles. Such coronas have been formed by mixing the different nanomaterials with plasma, and further incubated with macrophages to assess their potential bloodstream clearance. Finally, a plasmid encoding GFP has been employed to assess which candidate provides the best gene transfection along with the least protein adsorption and subsequent macrophage uptake.

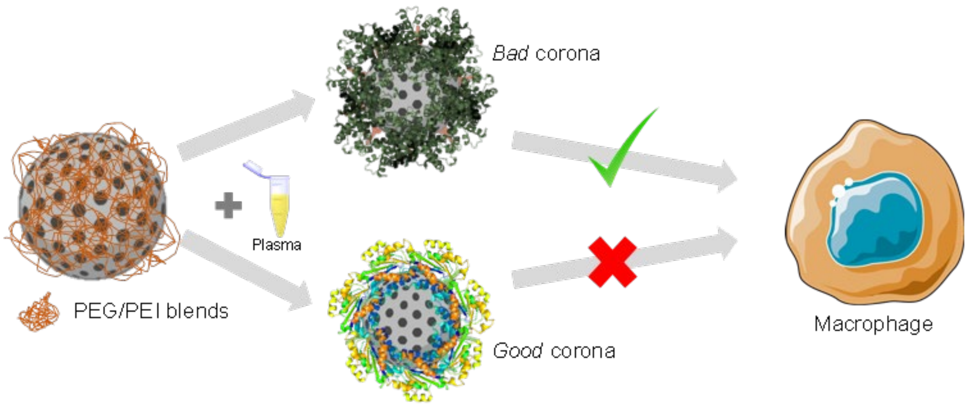

Figure 1 – Schematic representation of mesoporous silica nanoparticles coated with PEG/PEI blends and incubated with plasma to assess their interaction with macrophages

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Poly (methyl methacrylate) foaming in scCO2 and water

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Keywords: PMMA, scCO2, water, foaming, polymers.

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

Poly(methyl methacrylate) (PMMA) is a synthetic and amorphous polymer that belongs to the acrylate family. It presents high resistance to sunshine exposure, high impact strength, high scratch and shatter resistance, good degree of compatibility with human tissue, is a lightweight and exhibits favorable processing conditions and a reasonable resistance to chemicals [1]. Very promising application have been developed with PMMA in recent years through the polymer foaming with CO_2. The produced foams present very low thermal conductivity, which make them a great insulation material [2]. This work study foaming of PMMA with supercritical CO_2 in different conditions to obtain nanoporous polymers. Also, recent research showed no PMMA modification under hydrothermal conditions [3], so the foaming process is carried out in the aqueous media to improve the cell number and reduce the cell size.

Foaming was carried out in High-Pressure foaming unit HPF-700. PMMA and water in different ratios were placed in a high-pressure tube autoclave and CO_2 was also introduced in the system. The experiments were analyzed at different conditions such a pressure, particle size and time. The system was suddenly depressurized.

The foaming was achieved in all samples. The first results of the cell size distribution show similarities between the experiments with and without water, checking that this additive is working for foaming (Figure 1). Moreover, higher percentage of small cell sizes in the samples obtained in aqueous medium are obtained. Further experiments will be conducted to reach the best foaming conditions.

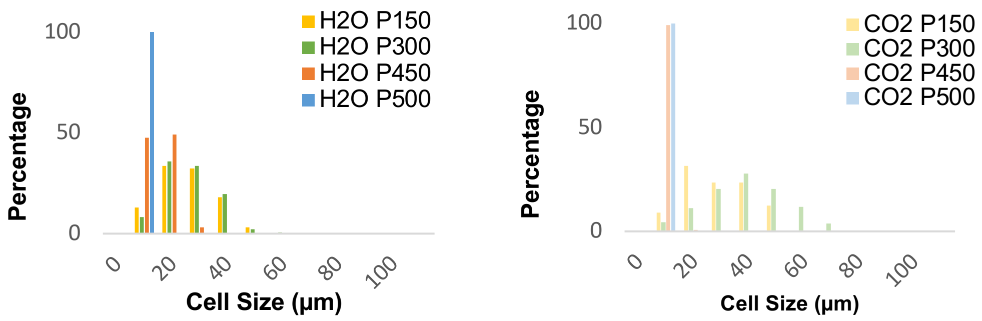

Figure 1 – Cell size distribution at different pressures: a) CO_2 and aqueous medium; b) CO_2

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PREVENTING MICROBIALLY - INFLUENCED CORROSION USING POLYOXOMETALATE - IONIC LIQUIDS

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Keywords: *polyoxometalate, ionic liquid, antimicrobial, microbially-influenced corrosion, metal corrosion.*

AMatS3.- Smart materials with advanced functionalities.

Corrosion of metals and other materials in the marine environment has an estimated global cost of $50-80 billion annually, representing severe problems for the oil & gas and maritime industries. Microbiologically influenced corrosion (MIC) accounts for a substantial portion of this corrosion, with sulfate-reducing bacteria (SRB) and methanogenic archaea (MA) being key contributors [1]. Conventional methods such as cathodic polarization have proven insufficient in mitigating the colonization of corrosive communities in real marine environments, requiring the development of alternative, broad-spectrum antimicrobial strategies to prevent such biofilm formation. Recently, molybdate has emerged as a potential alternative to traditional biocides and nitrate [2]. Our hypothesis is that polyoxometalate-based ionic liquids (POM-ILs) based on anionic polyoxomolybdates with tetraheptylammonium cations exhibiting antimicrobial and anticorrosion properties[3] could be suitable for coating and protecting metal surfaces. Here we show how POM-ILs $[(CH_3(CH_2)_6)_4N]_2[Mo_6O_{19}]$ and $[(CH_3(CH_2)_6]_4N]_4[Mo_8O_{26}]$ have demonstrated significant antimicrobial activity at microgram per millilitre (µg/mL) concentrations and metal surface-active biocidal activity (on brass, iron, aluminium, and steel). Furthermore, POM-IL-coated brass and iron coupons withstood extreme corrosive environments. These proof-of-concept results demonstrate that multi-functional POM-IL coatings offer promising prospects for mitigating MIC and addressing the challenges of marine biofouling by providing an acid-resistant hydrophobic protective layer and preventing biofilm formation. On-going research includes evaluating the effectiveness of POM-ILs against MIC-inducing microorganisms (e.g., SRB and MA), exploring the material-metal interactions, and evaluating the ability to prevent fouling in marine environments.

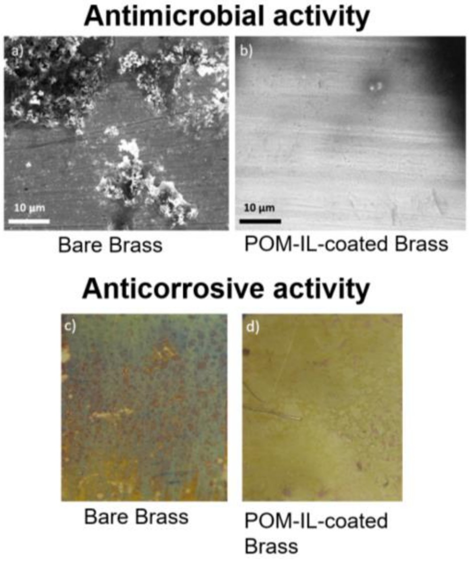

Figure 1: ESEM and photographic images of bare brass and POM-IL-coated brass exposed to a) microbial colonisation, and b) aqueous acetic acid (25%).

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Simulaciones de un micro posicionador y diseño de PCB para la medición de SQUIDs

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En este trabajo, presentamos el diseño y fabricación de un microposicionador [1] basado en dos enfoques complementarios. El primero emplea actuadores capacitivos para implementar movimiento en el plano x-y [2]. Por otro lado, se utilizarán materiales piezoeléctricos compatibles con CMOS para controlar el desplazamiento a lo largo del eje z [3]. Aquí presentamos simulaciones preliminares realizadas con COMSOL Multiphysics que nos permiten afinar los parámetros geométricos del posicionador considerando diferentes tipos de materiales. Además de eso, se utilizan simulaciones para estimar la resistencia, el estrés de Von Mises, las fuerzas de corte, las fuerzas de torsión y la constante elástica que sirven para calcular el desplazamiento efectivo final y la respuesta del dispositivo. Los micro posicionadores resultantes se combinarán con sensores magnéticos ultrasensibles como los nanoSQUID (Superconducting QUantum Interference Devices) [4]. De esta forma, será posible desplazar muestras nanométricas en las cercanías de las regiones más sensibles del nanoSQUID, para realizar escaneos de imágenes magnéticas y mediciones de referencia. En este póster presentamos los avances realizados hasta el momento en este trabajo de tesis doctoral.

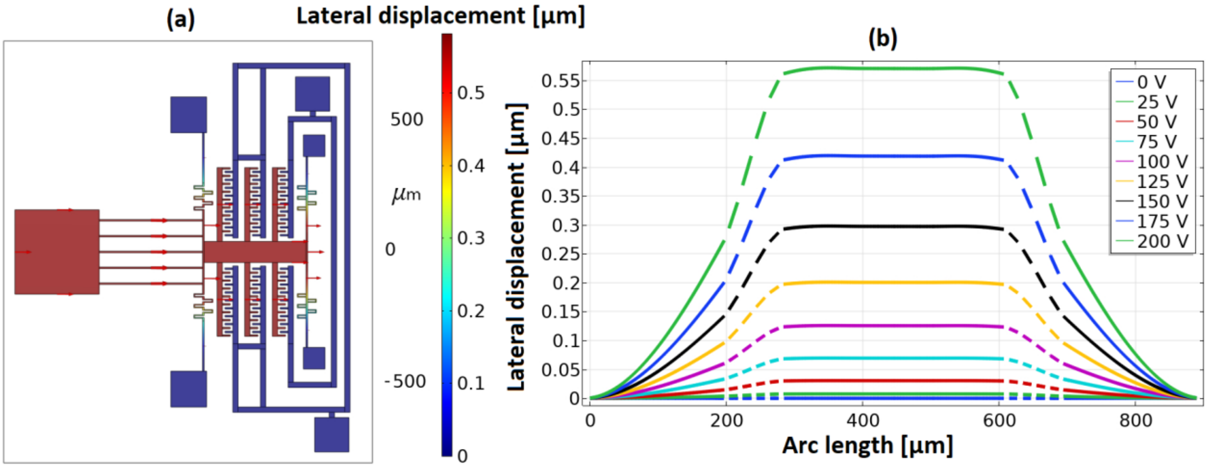

Figura 1. Simulación del desplazamiento de un brazo del dispositivo usando el principio de un acelerómetro capacitivo en Comsol Multiphysics (a) Desplazamiento para 200 V. (b) Longitud de arco en función del desplazamiento lateral para varios voltajes entre $0 \leq V \leq 200$ [V].

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SMART BONDLINES USING ULTRASONIC GUIDED WAVE INSPECTION

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Keywords: *structural health monitoring, multimaterial, adhesive bondline, ultrasonic guided waves, automotive.*

European countries are facing a challenge for greenhouse gas emission reduction, and, in this sense, electric mobility is key to meet the EU aim of carbon neutrality by 2050. To improve vehicle efficiency accelerating the electrification of the mobility, the aviation, railway, and automotive industries are pushing the development of lightweight structures.

Multi-material solutions combining composites and metals has arisen as a promising alternative for lightweighting while preserving required mechanical performance. However, it does not come without challenges. The metal-composite joint is usually adhesively bonded, creating a critical region where fatigue failure is a major concern. Furthermore, these joints are usually placed in hard-to-access locations. The integration of monitoring capabilities to track the integrity of the bond line would ensure safety while optimize maintenance and repair activities during the service life of the asset.

In LEVIS project (H2020-101006888), we have developed a monitorization system based on active ultrasonic guided waves (UGW) inspection using a numeric-experimental methodology to train damage prediction models with physics-informed synthetic data. Initially, the feasibility of measuring the progression of debonding defects was shown first in aluminium and CFRP coupons, with subsequent validation of finite element (FE) models. Then, an algorithm to detect debonding in the component was trained with synthetic data and demonstrated against experimental tests.

Ongoing work in the LEVIS project aims to combine structural health monitoring systems with component finite element simulation strategies. This integration will not only enable the diagnosis of structural failure but also the prognosis of the remaining useful life, facilitating real-time decision-making.

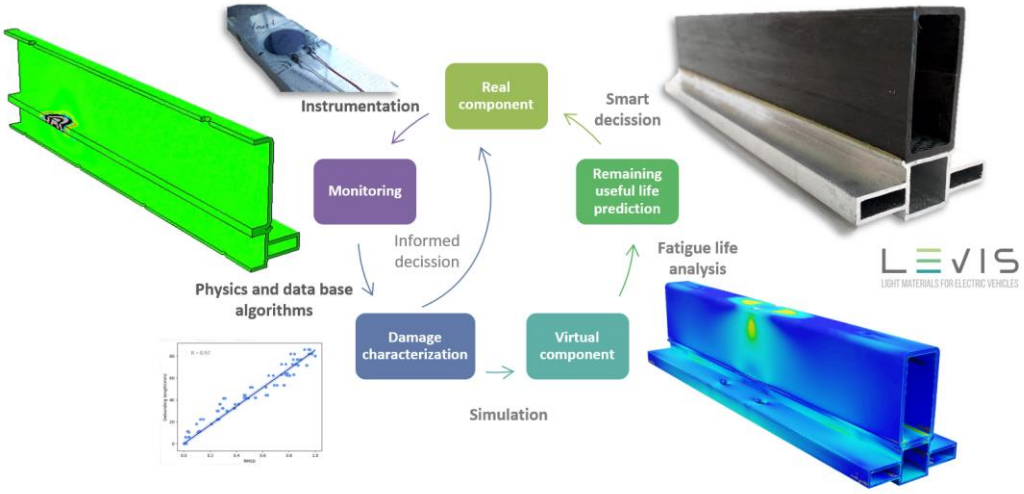

Figure 1. Structural health monitoring concept applied to the internal beam of a battery box.

Structure-property relationships in the antimicrobial activity of POM-peptide hybrids

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Keywords: *polyoxometalate, hybrid, antimicrobial, biofilm*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: NO

Antimicrobial resistance (AMR) has been recognized by the World Health Organization (WHO) as a major global threat. Among other measures, the WHO has emphasized that high levels of cleanliness among health professionals, medical instruments, and local environment is paramount to preventing the spread of infections and limiting antibiotic resistance. Consequently, there is an immediate need for alternative broad-spectrum antimicrobial materials to be used in compromised environments.

In our group we have recently shown that covalent hybrid materials based on polyoxometalates and synthetic antimicrobial peptides exhibit antibacterial and antibiofilm activities that are higher than the separate components.[1][2] Our objective in this project is two-fold. First, we aim at gaining insight on the role of reactive oxygen species in the antimicrobial activity of these materials by changing the main redox active center in the polyoxometalate –Mn (III) or Fe (III). Second, we will tune the POM-peptide molar ratio by using dendritic structures in the covalent hybrid in order to increase the activity (Figure 1).

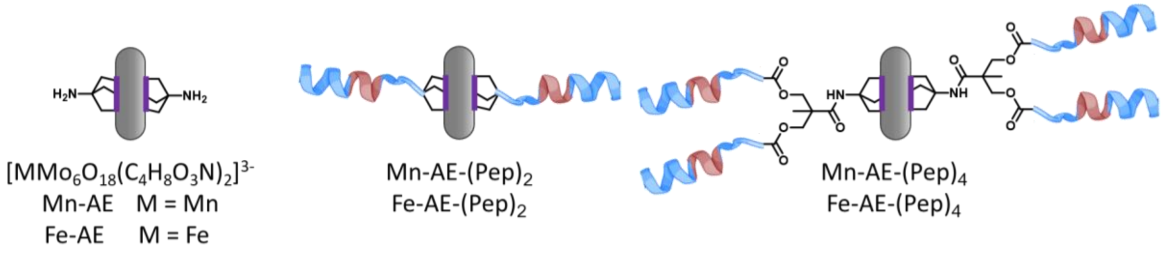

Figure 1 – Overview of the POM-peptide hybrids based on the Anderson Evans (AE) structure. Created with BioRender.com.

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Study of new materials for electromagnetic shielding in the frequency range of 5G technology

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Keywords: *electromagnetic shielding, 5G technology, MXene, bidimensional materials*

The 5G technology is having a significant impact on the communication industry. One of the 5G challenges is the design of new shielding materials able to reduce electromagnetic interferences (EMI) that allow 5G to coexist with other technologies.

Traditional metal shields can effectively attenuate EMI generated by 5G applications, but they generally have some drawbacks, such as lack of flexibility, high weight and volume, or low corrosion resistance. A new 2D material family of transition metal carbides or nitrides known as MXene with unique sets of properties has attracted growing attention for EMI shielding applications [1]. MXene material show excellent metallic conductivity, which is the highest among synthetic 2D materials because of their electron density near the Fermi level (EF) [2]. In this study, $Ti_3C_2T_x$ MXene was synthesized by a minimally intensive layer delamination (MILD) method from Ti_3AlC_2 precursor (MAX phase) [3].

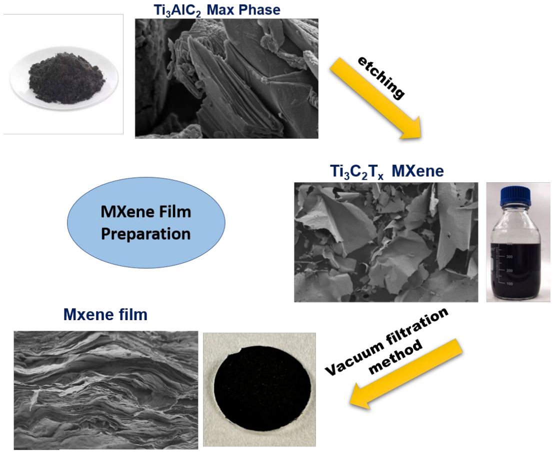

Figure 1 – MXene Film synthesis

Flexible MXene thin films (~8 μm) were obtained from aqueous $Ti_3C_2T_x$ dispersions by vacuum-assisted filtration (VAF) method. The dense arrangement of MXene nanosheets in the films contributes to enhance shielding effectiveness (SE). Previous studies found that the MXene flakes tend to degrade in humid air [4]. Nevertheless, the stability of MXene films and the effect on the SE of these materials remains largely unexplored. This contribution is focused on the stability and degradation of MXene films in a humid atmosphere and its impact on shielding effectiveness performance. The shielding effectiveness is measured with an innovative method that makes it possible to extend the frequency limit defined by the standard ASTM 4935-18 for measuring the electromagnetic shielding effectiveness of planar materials. Therefore, it is possible to determine the SE parameter of these new materials in the FR1 5G frequency region (up to 7.125 GHz). The results obtained demonstrate significant and flatness responses compared with other alternative shielding materials.

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Surface Stabilisation of the High-Spin State of Fe(II) Spin-Crossover Complexes

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Keywords: *spin-crossover complexes, spin-state transition, X-ray photoemission spectroscopy, magnetic susceptibility, surface effects*

Indicate one of the following areas:

AMatS3.- Smart materials with advanced functionalities.

Temperature dependent X-ray photoemission spectroscopy (XPS) has been employed to examine the Fe 2p and N 1s core levels of the studied Fe(II) spin crossover (SCO) complexes of interest, namely: $Fe(phen)_2(NCS)_2$, $[Fe(3\text{-}Fpy)_2\{Ni(CN)_4\}]$, and $[Fe(3\text{-}Fpy)_2\{Pt(CN)_4\}]$. The changes in the Fe 2p core-level spectra with temperature indicate spin state transitions in these SCO complexes, which are consistent with one's expectations and the existing literature. Additionally, the temperature dependence of the binding energy of the N 1s core-level provides further physical insights into the ligand-to-metal charge transfer phenomenon in these molecules. The high-spin fraction versus temperature plots reveal that the surface of each of the molecules studied herein is found to be in the high-spin state at temperatures both in the vicinity of room temperature and below their respective transition temperature alike, with the stability of the high-spin state of these molecules varying with the choice of ligand.

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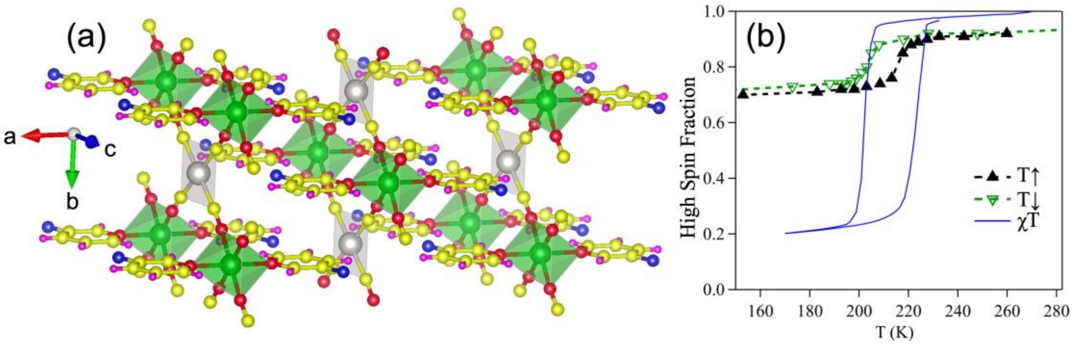

Figure 1: (a) Ball-and-stick model of the 2D Hofmann-like $[Fe(3\text{-}Fpy)_2\{Ni(CN)\}_4]$ with the Fe (green), Ni/Pt (silver), N (red), C (yellow), F (blue), and H (purple) atoms. (b) Normalized high-spin fraction of $[Fe(3\text{-}Fpy)_2\{Ni(CN)\}_4]$, extrapolated from XPS (black and green triangles) and magnetic susceptibility measurements (blue curve), as a function of temperature providing clear evidence of the spin-state transition.

SYNTHESIS, ELECTROCHEMICAL AND PHOTOLUMINESCENT PROPERTIES OF ALKALINE EARTH-TETRAZOL COORDINATION COMPLEXES AND POLYMERS

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Keywords: *Synthesis, Ae-Tetrazole, Coordination polymers (CP), Coordination Complexes (C) Photoluminescent property, Electrochemistry. X-Ray Study.*

Alkaline earth-tetrazole polymers were synthesized via in-situ transformation of the azide-nitrile cycloaddition reaction, employing alkaline earth (Ae) salts under hydrothermal conditions[1]. These polymers exhibit a 1D coordination polymer (1D-CP) structure composed of ribbons of tetrazole ligands, representing a recurrent example of such polymers in crystalline form. The crystal structures display a complex three-dimensional hydrogen-bonded network, accompanied by pi-stacking interactions involving coordinated water molecules within the 1D-CP. A topological study, along with Hirschfeld Surface analysis, confirms the dominant role of N...H/N...H and N...N contacts in the crystal structure networks.

Voltammetric analysis of three synthesized complexes reveals quasi-reversible reduction waves attributed to the reduction of Ae^{+2}/Ae and irreversible reduction peaks corresponding to the ligand. Additionally, irreversible oxidation peaks are observed and assigned to the oxidation of the tetrazole ring.

The fluorescence properties of three polymers were investigated at room temperature using emission spectra obtained at a consistent excitation wavelength[2]. Excitation of the samples led to similar fluorescence emission spectra, with the emission maximum ranging from approximately 360 to 380 nm, likely associated with the electronic transitions π-π* / π*-π* of the aromatic ring of the ligands.

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AMatS
2ND CONFERENCE ON
ADVANCED MATERIALS IN SPAIN
NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

The Design of Polypeptide-Based Nanoconjugates as Advanced Theranostics

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Keywords: *polypeptide-drug conjugates, rational design, theranostic, photodynamic therapy, cancer*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

INTRODUCTION: Synthetic polypeptide-based nanomedicines represent highly versatile, advanced therapeutic platforms, with multiple examples currently under clinical evaluation and polypeptidic drugs (Vivagel® and Copaxone™) achieving market approval [1]. As a drug delivery component, imaging represents a crucial means of improving nanomedicine-based therapy by optimizing patient stratification/treatment and accelerating the development/translation of personalised nanomedicines [2]. Theranostics combines therapeutic and diagnostic components into a single agent, providing real-time monitoring that can address remaining challenges in the field [2,3]. Introducing a porphyrin group can afford disease monitoring as part of theranostic approaches. Porphyrins are robust organic compounds bearing interesting photophysical properties, such as their attractive absorption and emission [3], and have been used for various applications that include diagnostic (e.g., fluorescence or magnetic resonance imaging [4]) and therapeutic (through photodynamic effects [5]) uses. Using two-photon fluorescence lifetime imaging, Yeh et al. demonstrate that subcellular localization can be determined based on differences in porphyrin fluorescence lifetime properties in the cell membrane and the cytosol [6].

RESULTS AND DISCUSSION: In this study, we exploited well-defined biodegradable polypeptide-based architectures prepared using N-carboxyanhydride ring-opening polymerized (NCA-ROP) [3,7] to obtain four-armed polyglutamic acid (PGA) constructs that self-assemble to yield stabilized supramolecular nanostructures with therapeutically-relevant properties [7]. Employing porphyrins as a core supports intrinsic imaging properties due to their photovoltaic properties [6]. Deprotection steps ensured the complete removal of protecting groups without racemization. This approach has obtained structures with different characteristics depending on the number of PGA units, going from cylindrical to spherical. They can be combined with imagen and photodynamic therapy using this characteristic because they also have different circulation times in the body and accumulation in the cells. Biological evaluation of these novel architectures has highlighted their robust imaging and photodynamic therapy potential.

Acknowledgments: This work has been supported by Pol@Mats (MFA/2022/065), by European Research Council (ERC-PoC-PolyBraint), APOST and AECC. Part of the equipment employed in this work has been funded by Generalitat Valenciana and co-financed with FEDER funds (PO FEDER of CV 2014–2020).

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THIN FILM NANOCOMPOSITE (TFN) MEMBRANES INCORPORATING FeMn NANOPARTICLES FOR WATER DESALINATION

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Keywords: *thin film nanocomposite (TFN) membranes, magnetic nanoparticles, reverse osmosis, water desalination*

Reverse osmosis (RO) is the most prevalent membrane desalination technology in industrial applications. The membranes used in RO pose several challenges, such as using more environmentally friendly fabrication methods and membrane recycling or extending their lifespan (preventing fouling and improving resistance to cleaning treatments) [1].

Thin film composite (TFC) membranes are the most widely employed membranes for water desalination. They consist of a porous polymeric support, providing them with mechanical strength, and a thin-film selective layer of polyamide which enables the separation of water molecules from salts [1]. TFC membranes were synthesized using interfacial polymerization (IP) methods. The polyimide porous support was synthesized via phase inversion. The thin film selective layer was synthesized through IP using m-phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers. After IP, membranes were heat-treated at 80°C to promote the chemical cross-linking of the polymeric chains boosting the selective properties of the layer.

This study aims to assess the effects of incorporating magnetic nanoparticles (MPN) in the thin film layer on permeate flow and membrane rejection for RO applications. Ultimately, it seeks to assess the impact of these nanoparticles (NP) on membrane performance and efficiency during RO discontinuous cycles lasting over 3 hours.

Thin film nanocomposite (TFN) membranes containing FeMn NP were prepared through IP using the same conditions as in TFC membranes. FeMn NP were dispersed by sonication in the aqueous phase during IP. The polymeric support was impregnated with this dispersion so that, after the addition of the TMC solution and subsequent IP, the MPN became embedded within the selective layer (as depicted in Fig. 1). Water permeance and salt rejection were evaluated for the TFCs and TFNs, before and after exposure to chlorine.

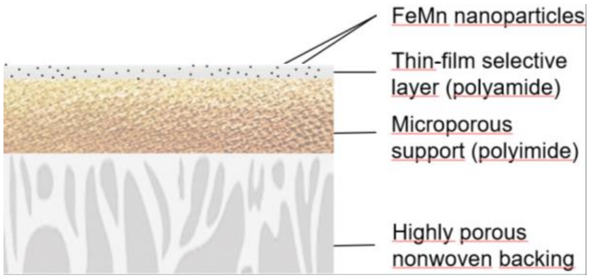

Figure 1. TFN membrane scheme

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Tuesday, November 14th - LA1

LA 1 Large Scale Production of Monolayer Graphene: From the lab to the fab and to the consumer market

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After more than a decade and tens of thousands of publications, graphene produced by chemical vapor deposition on copper foils is still at the top of the league in terms of production cost, productivity and quality, particularly for large-scale production of monolayers on insulators. I will review the principle of these techniques, their advantages and prospects, and then present the use of this process for the industrial production of these films with quality control.

I'll show how the implementation of synthesis techniques for this material, based on microelectronics processes, enables it to be mass-produced at low cost, using clean-room processes based on printed electronics.

I will also present recent work on the realization of consumer products based on these materials, where we are developing an electronic strip concept based on a graphene/polymer film, a new material for the life sciences.

I will also present recent works on the realization of consumer grade products based on these materials where we are developing a concept of an electronic strip based on graphene/polymer film a new material for Life Science. Graphene sensors will be described, and in particular I will show how they can be connected and powered by a simple link to a smartphone. They can be easily coupled to a digital monitoring solution via the smartphone that will improve field diagnosis and chronic disease monitoring.

Graphene technology: CVD-growth under high precursor flux and its transference.

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Keywords: *graphene, CVD growth, 2D transfer, cold-wall reactor*

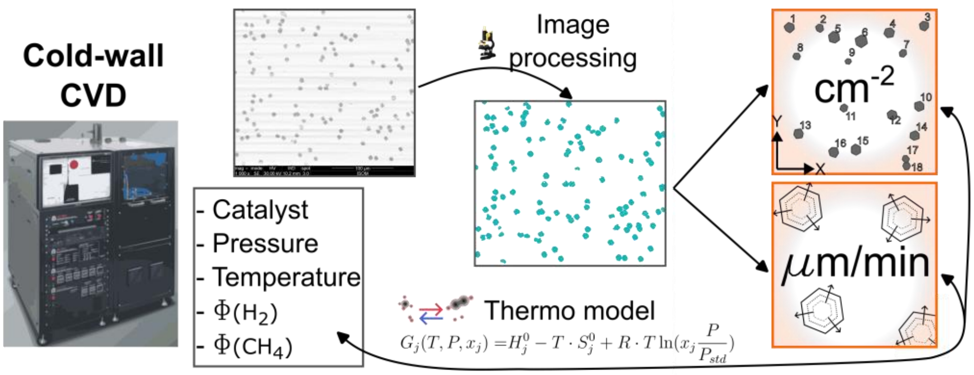

Figure 1 – Optimization of graphene growth

Chemical vapour deposition (CVD) has proven to be the best technology for achieving high-yield, electronic-grade graphene. Although most CVD studies are based on lab-scale hot-wall reactors, industrial applications of graphene in electronics require its production by industry-ready cold-wall reactors, which are capable of growing material under high precursor flux conditions. Therefore, we present a comprehensive study [1] to translate the well-known thermodynamic configuration of hot-wall reactors onto our commercially-available cold-wall reactor (Aixtron BMPro). In this study, the thermodynamic parameters and catalyst treatments that affect the growth dynamics and the material quality in a cold-wall reactor are presented (Figure 1). After each material fabrication run, the lateral growth rate and the nucleation density, obtained by scanning electron microscopy and imaging techniques, are introduced into a thermodynamic model. This information can be applied to modify the growth conditions and establish a material improvement method. The quality of the single crystals obtained by this method has been confirmed using Raman mapping and electrical measurements, ensuring high-quality material at moderate growth times. Finally, we propose a well-proven method to transfer [2] the obtained material onto the final application substrate.

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Bridge engineering for atomically precise graphene-based nanoarchitectures

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Abstract:

Bottom-up nanoarchitectonics has demonstrated the capability to control structural parameters of nanomaterials with atomic precision. The surface-assisted synthesis of graphene-based one-dimensional nanostructures à la carte distinctly illustrates the power of this concept. However, despite impressive advances in the synthesis of 1D homostructures, advancing in structural complexity faces major challenges. A clear example is the extension of the on-surface strategy to two-dimensional structures, where examples of long-range ordered nanoarchitectures are very limited. Recently, we have developed an effective strategy to maximize long-range order in 2D, by synthesizing graphene nanoribbon to use them as 1D building blocks that are laterally coupled in a second step [1].

Here we show how molecular engineering of the coupling bridges enables the extension of this method towards the synthesis of more complex 2D nanoarchitectures.We will show an example where the introduction of phenyl groups in the bridges brings tunability of the quantum electronic coupling and the corresponding in-plane electronic anisotropy [2]. In a second example we extend the method to mix two intercalated components to lead to the formation of lateral heterostructure superlattices where the junction is defined with atomic precision [3].

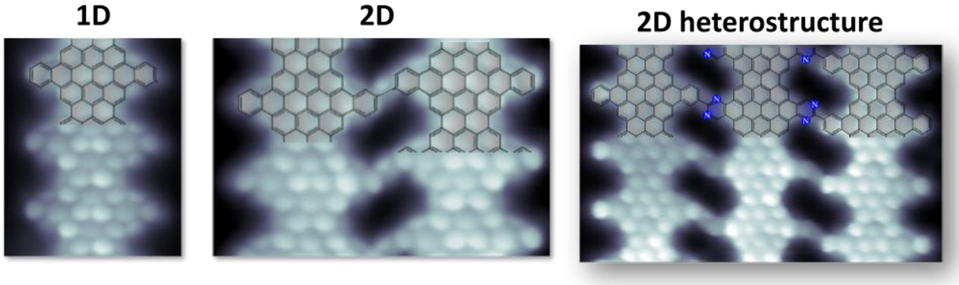

Figure: Bond-resolved STM images of a 1D graphene nanoribbon (left); coupled nanoribbons forming the unit of nanoporous graphene; a trimer forming the basic unit of a lateral heterostructure superlattice.

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SCALABLE PROCESSING OF LARGE AREA MoS_2 COATINGS BY NEBULIZATION

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Keywords: *2D material, liquid-phase exfoliation, 2D inks, spray-coating, MoS2, photodetector, FETs*

AMatS1.- **Graphene and other 2D materials**.

During the last 20 years, diverse synthetic approaches and processability procedures have been researched for the wide branch of this family of 2D materials, since 2004 when Geim and Novoselov discovered the bidimensional material world. Nowadays, some devices based on 2D materials have been tested proving them in different applications: field effect transistors (FET), strain gauges, photodetectors, transparent conductive electrodes, supercapacitors.[1] However, the fabrication of many of them is artisanal and difficult to scale-up. Thus, liquid-phase exfoliation (LPE) [2] or electrochemical exfoliation (EE) [3] were developed, which enable mass production of colloidal dispersions of 2D materials (2D inks). With these 2D inks, various deposition techniques can be tested, such us blade coating, spray-coating, spin-coating, ink-jet printing, screen printing or roll to roll processing. Although, for large-area electronics and coatings the most powerful ones are spray-coating and roll to roll processing. Therefore, our group has developed an array of 2D inks (graphene, alpha-Ge, MoS_2, h-BN…) by LPE and our own deposition set-up based on nebulization that is a step up of the spray-coating technique, with lower and more uniform droplet size and affordable and easily scalable nebulizer. This work presents a green solvent-based, simple, cheap, and scalable procedure to produce MoS_2 coatings and thin films for solar cells,[4] FETs,[5] and photodetector applications;[6] due to the semiconducting and optical behavior of MoS_2.

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FABRICATION OF 2D MATERIALS-BASED NANOARCHITECTURES VIA INNOVATIVE CVD PROCESSES

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Keywords: *borophene, graphene, hBN, chemical vapor deposition, STM, ARPES, DFT.*
AMatS1.- Graphene and other 2D materials.

The abilities to combine complementary two-dimensional (2D) materials and to introduce modifications at the nanoscale open compelling routes to engineer the material's properties and grant novel functionalities [1,2]. In this talk, I will introduce two innovative chemical vapour deposition (CVD) processes enabling flexible growth of atomically thin 2D materials and related heterostructures, such as borophene, hexagonal boron nitride (*h*BN) and graphene.

Specifically, the use of diborane as precursor gas yields large single-crystalline borophene domains (*i.e.*, an atomically thin layer made of elemental boron) on distinct metal supports. Subsequent addition of borazine as precursor in the process allows synthesizing *h*BN conjointly with borophene, which can selectively form lateral or vertical heterostructures. When combined laterally, borophene and *h*BN form uniform covalent lateral interfaces, while the vertically stacked configuration result in van der Waals structures that protect borophene from immediate oxidation [3]. On the other hand, the use of a single molecular precursor (borane tetrahydrofuran) providing boron and carbon enables the fabrication of 2D arrays of boron substitutional species in graphene. These are formed due to segregation of the boron atoms, which is guided by the naturally occurring moiré superstructures in Ir(111)-supported graphene [4].

Our findings are based on a comprehensive surface-science approach that combines atomic-scale and surface-averaged characterization techniques (*i.e.*, scanning tunnelling microscopy and spectroscopy STM/STS, low energy electron diffraction LEED and x-ray photoemission spectroscopies XPS/ARPES), together with first-principles calculations that provide insight into the material's structure, chemical and electronic properties, and interfacial interactions.

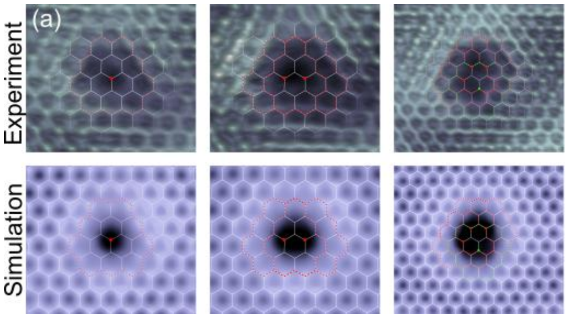

Figure 1 – Comparison between experimental and simulated atomically resolved STM images of single and multiple substitutional boron atoms in Ir-supported graphene.

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TOWARD SELF-DRIVING LABORATORY FOR THE DESIGN OF MULTIFUNCTIONAL NANOCOMPOSITES INVOLVING 2D MATERIALS

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Keywords: *nanocomposite materials, materials acceleration platforms, additive manufacturing*

AMatS1.- Graphene and other 2D materials.

Advanced polymer nanocomposites are relevant to a broad spectrum of applications, from clean and efficient industrial separations through innovative medicine to safe commodity products with low-impact life-cycles. We specifically focus on sustainable and multifunctional nanocomposites, which incorporate bio-based polymer matrixes and multiple advanced functional components such as 2D materials and/or metal-organic frameworks. Formulating the composition of such nanocomposites tuned to a specific application poses a significant challenge as they need to include the appropriate components to ensure desired performance while simultaneously addressing constraints regarding the physicochemical compatibility between them as well as the overall dependence on the processing involved. We are streamlining this process by the development of a dedicated material acceleration platform (MAP). The MAP is a closed-loop experimental setup where laboratory work related with preparation and characterization of samples is performed by a robot while machine learning algortihms dictate what experiments to make in order to achieve desired results with minimal number of experiments. Unlike other emerging MAPs that work with solution or thin-film chemistries, our MAP focuses on thermoplastic materials, which are processed in a pelletized form and require solid specimens for property testing.

Our presentation will introduce the concepts behind our nanocomposite MAP and summarize the recent progress in its development, which for far have included (i) an automated twin-screw extrusion process for nanocomposite preparation, (ii) a nested Bayesian optimization loop for 3D printing of testing specimen executed on a pellet 3D printer farm, (iii) a collaborative robot-operated analog Charpy impact test instrument and (iv) an outer Bayesian optimization loop for navigating the nanocomposite formulation space. Such organization of the MAP allow fairly easy extension to other properties such as tensile tests, thermal and electric conductivity etc, which are the subjects of on-going work.

Curcuminoids as single units and in assemblies: from nanowires in graphene devices to 2D materials

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Keywords: *molecular design, PAH-based CCMoids, GFETs, nano-gapped graphene-based three-terminal devices, 2D molecular systems, exfoliation, deposition, electronic properties*

Indicate one of the following areas:

AMatS1.- Graphene and other 2D materials.

At FunNanoSurf we work with curcuminoids (CCMoids), a family of linear and conjugated organic molecules with a broad spectrum of application in nanoscience and nanotechnology. We focus our efforts on molecular design, characterization and transfer to substrates, including the latter from rigid materials, fiber-based arrays and devices.[1] Taking advantage of their chemical versatility, we are able to use CCMoids as individual building blocks (nanowires), or as molecular platforms (1D-3D systems).[2-5] In particular, this work aims to highlight our latest single electron transport studies performed with CCMoids as nanowires embedded in graphene. Also, how we can optimize, through molecular design, their coordination ability and create 2D systems that can be exfoliated and deposited on substrates/transistors. This talk briefly summarizes our most relevant findings to give an overview of possible and future applications of CCMoids in molecular electronics.

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NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

GRAPHENE & 2D CRYSTAL POLARITONICS ENABLED BY SURFACE ACOUSTIC WAVES

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Keywords: *graphene, 2D crystals, polaritonics, surface acoustic wave*

AMatS1.- Graphene and other 2D materials.

Surface acoustic waves (SAWs) are especially well suited for modulating graphene and other 2D materials as their strain and piezoelectric fields are strongly concentrated at the surface of the piezoelectric substrate that supports the 2D crystal. Moreover, many 2D materials are themselves piezoelectric, enhancing the capabilities of strain modulation. The interdigital transducer (IDT) technology permits to excite the SAWs electrically to generate strain locally at very high frequencies, as shown in Figure 1, that can modulate dynamically the optical and vibrational properties of 2D crystals [1]. Moreover, SAWs also provide an outstanding platform for confining light at the nanoscale, exploiting the strengthening of its associated electric field, which results in enhanced light-matter interactions or quasiparticles. Thus, the strain field of the SAW can act as a virtual optical grating allowing to launch propagating polaritons in unpatterned 2D materials and van der Waals heterostructures, such as surface plasmon-phonon polaritons in graphene [2] and graphene/h-BN systems [3], the latter also supporting hyperbolic modes, as well as surface plasmon-exciton polaritons (or plexcitons) in 2D semiconductors (for example MoS_2 and black phosphorus) on thin metal layers [4]. These SAW-mediated architectures pave the way for implementing nanophotonic devices, where polaritons can serve as ultrafast and low power signal carriers. Furthermore, they can also act as ultrasensitive biosensors capable of fingerprinting ultrathin biolayers with a sensitivity down to the monolayer limit, as tested with a protein bilayer or a peptide monolayer [5]. This paves the way for the development of advanced SAW-assisted lab-on-chip systems combining the existing SAW-mediated physical sensing and microfluidic functionalities with the chemical fingerprinting capability of this novel SAW-driven polaritonic approach.

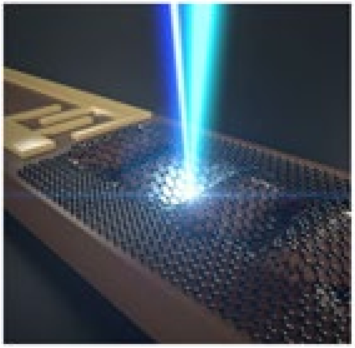

Figure 1 – An IDT generates a SAW that modulates the graphene or 2D crystal

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1D nanostructures with layered cobalt dioxide and their electrical properties

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Keywords: *layered cobalt dioxide, 1D nanostructures, transmission electron microscopy, electron energy-loss spectroscopy, crystal conversion*

Layered cobalt dioxide in bulk form is only meta-stable and its synthesis is mostly obtained from de-intercalation of Li_xCoO_2 and similar structures [1] or by intercalation in the form of misfit-layered compounds (MLCs) [2]. Crystal structures, which are unstable in bulk form, may have a stable form if its size is reduced to the nano-regime. For such nanomaterial synthesis routes, the starting material is either a mixture of the individual elements or the corresponding bulk structure. Recently, we introduced a novel synthesis method based on a crystal conversion process, which parts from a bulk structure with a different crystal structure [3]. Here, we will present the in-depth electron microscopy analysis of nanotubes and scrolls based on layered CoO_2 that have been obtained using this method with two different starting compounds [3,4].

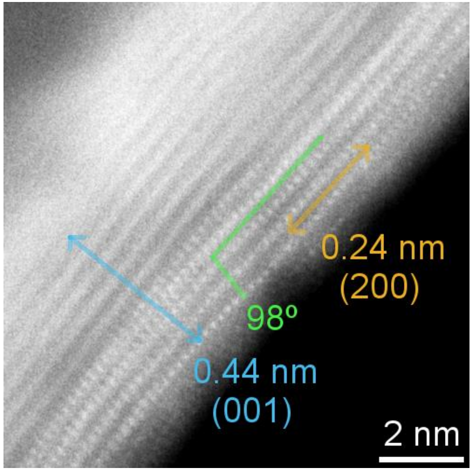

Figure 1 – HRSTEM image of CoO_2 nanoscroll with lattice distances marked.

The process starts from bulk material with a quasi 1D crystal structure, e.g. $Sr_6Co_5O_{15}$ [3] or $Ca_3Co_2O_6$ [4], which is treated in a hydrothermal process in basic environment. This environment renders the structure unstable and dissolves the Sr or Ca ions leaving cobalt oxide chains behind. These chains then bind to nanotubular or scrolled forms.

The resulting products are studied by electron microscopy and spectroscopy and related techniques. The electronic properties of the nanotubes are analyzed in detail on the individual nanotube level. In case of Sr-based bulk precursor, nanotubes of a misfit-layered compound Sr_xCoO_2 – CoO_2 are observed, which is Sr-deficient compared to the nanotubes obtained by a classical synthesis route [2]. In the case of Ca, nanoscrolls made of pure layered CoO_2 are obtained, see high-resolution scanning transmission electron microscopy image in Figure 1. The scrolls all possess a similar size and wall width suggesting that the CoO_2 stabilization occurs under specific circumstances.

The Sr_xCoO_2 – CoO_2 nanotubes possess an extremely high ampacity (10^9 A cm^{-2}) and an extraordinary breakdown power per channel length (P/L 38 W cm^{-1}) [3]. The results on structure and properties show that the crystal conversion route is promising to synthesize structures unstable in its bulk counterpart.

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DIFFERENT APPROACHES TO OBTAIN MATERIALS BASED ON MWW ZEOLITES LAYERS AND MgAlCe HYDROTALCITES

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Keywords: MWW zeolites, LDH

AMatS1.- Graphene and other 2D materials.

The development of sustainable and efficient chemical processes is one of the highest priorities in contemporary society. For this reason, using heterogeneous catalysts with the reusable capability of performing such processes in a single step could avoid the isolation of intermediates and the recovery and disposal of by-products and solvents. For this purpose, this study aims to link different components in the same structure to benefit from the advantages and physicochemical characteristics of each component and to generate new properties due to the synergy and cooperative effects established between them.

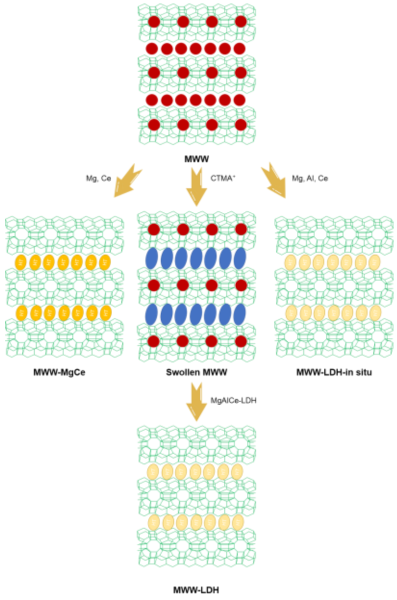

Figure 1 – Scheme of the different synthesis strategies.

Lamellar materials are crucial to obtaining these multifunctional catalysts [1]. These materials are versatile in modifying their morphology and textural properties by altering the order and spatial arrangement of the individual sheets that form them. Likewise, their composition and reactivity can be changed by including organic or inorganic compounds on the surface and interlamellar space [2].

Mg-Al oxides are one of the most widely used solids in catalysis. This is due to their number of basic sites, high thermal resistance, and high specific surface area. In addition, Mg-Al layered double oxides (MgAl-LDH) are usually modified by incorporating a third atom. This could improve the catalytic properties and modify the acid-base sites [3].

In this work, we report different simple synthesis strategies to obtain new multicomponent materials considering the versatility of the lamellar MWW zeolitic materials to modify their morphology. The different materials have been characterised by Powder X-Ray Diffraction (PXRD), Chemical Analysis (ICP and EA), Solid State NMR, thermogravimetry and electronic microscopy.

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In Depth Investigations of Graphene Oxide Reduction via in-situ TEM

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Keywords: *2D Materials, Graphene Oxide, in-situ TEM, Thermal Reduction,*

Graphene oxide (GO) strongly attracts research interest due to its use as precursor material for graphene-based material and its high flexibility in terms of functional modification offering promising applications in numerous fields [1-5]. It is worth to mention that graphene oxide as well as reduced graphene oxide (rGO) have become two materials of abundant importance within the realm of 2D materials in general and chemically modified graphene in particular. Despite the efforts for investigating its atomic structure, which is critical for knowing its properties, several aspects remain unknown in particular the behavior of the physi-/chemi-sorbed and of the oxygen functional groups (OFGs) during GO reduction. Indeed, the processes taking place in the thermal reduction of GO into rGO are still not completely clear. In-situ TEM studies involving GO heating seem like an ideal method for achieving this goal [6]. Here we present two different approaches for studying, in depth, the GO reduction via in-situ TEM investigations: thermal reduction and Joule heating, see Figure 1. For achieving these comprehensive studies [7-8], we have performed HRTEM imaging and electron energy-loss spectroscopy (EELS) measurements and coupled (for the second of these studies) with electrical conductivity measurements. In both studies, we have identified the transformations of different oxygen functional groups, the desorption of physisorbed and chemisorbed water and the graphitization of the GO flakes. These in-depth analyses provide a detailed roadmap of the behavior of GO during its reduction and graphitization. All these findings improve the knowledge of this complex and heterogeneous material, which is crucial for the study of their physical and chemical properties and its future applications.

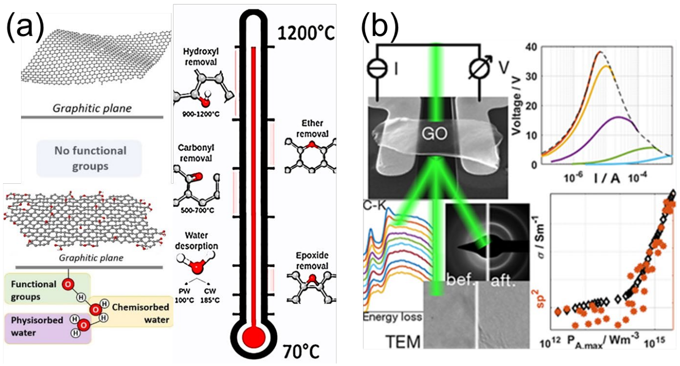

Figure 1 (a) General schematic on the main results of this study showing the reduction of GO via detailed in-situ heating TEM (HRTEM & EELS) [7]. (b) Reduction of GO via detailed in-situ Joule heating TEM (HRTEM, electron diffraction & EELS) studies and coupled with conductivity investigation by electrical measurements [8].

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New tools for Materials Science research at JEMCA in ALBA Synchrotron

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The integration of electron microscopes with synchrotrons has been a growing field of research and development in the recent years. The combination of these two powerful techniques has been pursued by scientists and engineers to enhance the capabilities and expand the applications of both instruments. The integration of these techniques facilitates breakthroughs in various scientific fields, including materials science, nanotechnology, biology, and energy research. With these ideas in mind, several institutions (ICN2, ICMAB, CSIC, UAB, IBMB, CRG, IRB and ALBA) have collaborated together in order to create the Joint Electron Microscopy Center at ALBA (JEMCA), in the ALBA synchrotron, which is one of the funding members of e-DREAM.[1] Up to now, two high-end transmission electron microscopes have been already installed - a Thermofisher Glacios cryo-TEM and a Thermofisher Spectra 60-300kV -, together with a focus ion beam Thermofisher Helios 5UX, while a third (S)TEM (devoted to in-situ experiments) will also be installed in the following years. Besides the researchers belonging to those institutions, external users will also have the opportunity to access this equipment through competitive open calls that will be periodically announced in the ALBA website.

The installed Spectra 300 is equipped with a double aberration corrector, a thermally-assisted field emission gun (X-FEG) with monochromator, a pixelated EMPAD detector, a 16-segment panther detector for differential phase contrast acquisitions, a high-sensitivity, windowless Super-X EDX detector system and a Continuum K3 Gatan Energy Filter with a CMOS and a retractable K3 direct-detection electron camera. This instrument is very versatile as it can be operated at 4 different high-tensions (60kV, 80kV, 200kV and 300kV), providing ultimate spatial and energy resolution: below 25meV (at 60kV) and 50pm (at 300kV). In this contribution, I will present the JEMCA infrastructure, I will describe the experimental possibilities offered by this new tool, showing some preliminary results obtained during the commissioning period, and also I will show how external users can apply to exploit it for their own research.

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LA 1 Intrinsic magnetic topological insulators in the family of 2D van der Waals compound $MnBi_2Te_4$

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Magnetic topological insulators (MTIs) are narrow gap semiconductor materials that combine non-trivial band topology and magnetic order. They host a number of exotic phenomena having potential applications. Previously, MTIs were only created by means of doping nonmagnetic TIs such as $(Bi_{1-x}Sb_x)_2Te_3$ with Cr or V atoms, however such an approach leads to strongly inhomogeneous magnetic and electronic properties of these materials, restricting the observation of important effects to very low temperatures. Recently, a stoichiometric 2D van der Waals (vdW) compound $MnBi_2Te_4$ was theoretically predicted and then experimentally confirmed to be the first intrinsic antiferromagnetic TI (AFMTI) [1-4].

The discovery of $MnBi_2Te_4$ opens a new field that focuses on intrinsically magnetic stoichiometric 2D vdW compounds: several $MnBi_2Te_4$-derived MTIs were synthesized right away [5,6], such as $(MnBi_2Te_4)\cdot n(Bi_2Te_3)$, $MnBi_{2-x}Sb_xTe_4$, $(MnSb_2Te_4)\cdot n(Sb_2Te_3)$, $Mn_2(Bi,Sb)_2Te_5$, and $MnBi_2Se_4$, that will also be discussed in the talk. As a result, $MnBi_2Te_4$ has been predicted to be a platform for realizing high-order topological insulator and superconductor states, Weyl semimetal phase, skyrmions, quantized magnetoeletric coupling, and Majorana fermions. Moreover, $MnBi_2Te_4$-based systems are predicted and/or observed to show 12 different types of Hall effect, some of them are fundamentally new, such as the layer Hall effect [7]. In $MnBi_2Te_4$/hBN vdW heterostructures, a stack of n $MnBi_2Te_4$ films with $C = 1$ intercalated by hBN monolayers gives rise to a high Chern number state, characterized by $C = n$ chiral edge modes [8], this number being as large as allowed by the vdW heterostructures growth technology.

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ELEVATOR PITCH
LA1

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Additive manufacturing of YSZ-based porous implants by Fused Filament Fabrication (FFF) for load-bearing applications

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Keywords: *YSZ powder, additive manufacturing, bone repairing, porous implant*

AMatS1.- Graphene and other 2D materials.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES

In the field of bone replacement and post-surgical issues, the ceramic 3 mol% yttria-stabilized zirconia (3-YSZ) is suggested as the material that fits better the mechanical requirements for bone regeneration in load-bearing applications. In this sense, the trend is to replace the minimum portion of the bone, and efforts are focused on manufacturing porous implants that will allow bone ingrowth in order to favor the natural bone-repair mechanisms. However, the use of zirconia for load-bearing applications is commercially nonviable partially due to the immature fabrication techniques of zirconia-based porous implants [1]. The advance in additive manufacturing (AM) techniques holds promise for the fabrication of implants, and yet zirconia has not been fully explored in this regard; scarce literature has been found in the additive manufacturing of 3-YSZ, even less in Fused Filament Fabrication (FFF), which has been rated as the AM technique with the highest translational potential and the lowest cost of production [2]. The possibilities of new and complex architectures (geometries and internal porosity) that these techniques introduce call for their application in 3-YSZ porous implants manufacturing. Despite the fact that 3-YSZ is a well stablished material for bone-related applications, mainly in dentistry, its use in bone repairing is not exempt from controversy because of its low-temperature degradation (LTD). The strong emergence of 2D materials and the unique properties that they provide to other materials has led to their research in all fields of material science, and implants are no exception. Regarding 3-YSZ, some 2D materials have been proven to decrease LTD. Moreover, their role in antimicrobial activity is well known, which is crucial for bone repairing since infections are the most common problem and causes of poor bone repair. For all these reasons, the evaluation of 2D materials incorporation in 3-YSZ implants is of relevance [3].

Due to the limited availability of an adequate 3-YSZ filament on the market for FFF, the results presented involve the design of a new 3-YSZ printable filament as foundation for future incorporation of 2D materials. Implants with different architectures will be presented and mechanically evaluated to understand how they influence the mechanical properties of this material. As a result, the potential of these 3-YSZ implants and the possibility of incorporating 2D materials will be discussed through the lens of personalized medicine.

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ELEVATOR PITCH
LA2

Dihydroxybenzenes as a thermal energy storage material.

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Keywords: *Isomers, Rotamers, Calorimetry.*

AMatS2.- Materials for Energy.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES

Abstract:

State-of-the-art calorimetric techniques have been used to characterize the three dihydroxybenzene: ortho- (o-dHBZ), meta- (m-dHBZ), and para- (p-dHBZ) isomers. Calorimetric studies reveal that o-dHBZ and m-dHBZ undergo the process of glassification. However, p-dHBZ exhibits an unavoidable tendency to crystallize. The new metastable phases observed by the calorimetric measurements in o-dHBZ could be related to the presence of intermolecular and intramolecular hydrogen interactions, while m-dHBZ formed only intermolecular bonds and no new transitions [1]. These results incite the curiosity to understand these compounds in detail through DFT calculations. In the results of relative conformational single point energy calculations, o-dHBZ maintains a difference in energy profiles of nearly 0.17 eV from the other two isomers. The difference between the energy profiles supports the hypothesis of interplay between intramolecular and intermolecular interactions in o-dHBZ. This is further validated by bond analysis between the monomer and dimer configurations of the o-dHBZ by exhibiting intramolecular H-bonds in former and only intermolecular H-bonds in the latter. The complex thermophysical behaviour observed for o-dHBZ can be accounted to substantial activation of intramolecular bonding in the liquid phase as well as in the resulting metastable phase observed in the calorimetric results. In terms of material design for energy, o-dHBZ offers a unique framework to precisely control the degrees of freedom where energy can be stored by making the use of assembly of ordered or disordered phases with their distinct physiochemical properties.

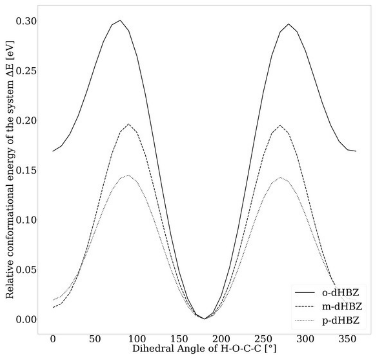

Figure 1 – Relative conformational energy of dihydroxybenzene rotamers.

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Exploring new magnetoelectric mutiferroics based on hybrid improper ferroelectric oxides: $Ca_3Mn_{2-x}Ru_xO_7$ and $Sr_{3-x}La_xSn_{2-x}M_xO_7$ (M= Cr, Fe, Mn)

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Keywords: *magneto-electric multiferroic oxides, Hybrid Improper ferroelectricity, neutron diffraction, synchrotron x-ray absorption spectroscopies, low energy consumption*
AMatS2.- Materials for Energy.

if you are interested in participating in the Poster Flash/Elevator Pitch session: **YES**

The search of multiferroic materials with magnetoelectric coupling near room temperature (RT) attracts enormous research attention due to the promising applications for ultra-low-power electronic devices. Hybrid improper ferroelectrics (HIFs) [1] are currently of great interest for the realization of RT multiferroelectricity with strong magnetoelectric coupling. Some of the latest HIF materials discovered belong to the family of $(AO)(ABO_3)_2$ Ruddlesden-Popper (R-P) perovskite oxides: $Ca_3Mn_2O_7$ and $Sr_3Sn_2O_7$. The former undergoes a structural phase transition (T_S=310 K) to a low-temperature orthorhombic polar phase [2] whereas the later exhibits both, ferroelasticity and ferroelectricity with a relatively low coercive field in single-crystals [3]. To extend the functionality of these materials, we have explored the possibility of inducing ferromagnetism by replacing either Mn or Sn with magnetic atoms. In this way, we have prepared $Ca_3Mn_{2-x}Ru_xO_7$ and $Sr_{3-x}La_xSn_{2-x}M_xO_7$ (M = Cr, Fe, Mn) compounds up to x=1.

The new compounds are single phase solid solutions and they adopt the orthorhombic $A2_1am$ polar structure of the parent compounds at RT [4]. Thus, the HIF mechanism is fully operational along the $Ca_3Mn_{2-x}Ru_xO_7$ and $Sr_{3-x}La_xSn_{2-x}M_xO_7$ series. Isothermal M(H) measurements suggest an enhanced ferromagnetism through the occurrence of spontaneous magnetization for Ru-doped $Ca_3Mn_{2-x}Ru_xO_7$ samples with $x \geq 0.3$ and, among $Sr_{3-x}La_xSn_{2-x}M_xO_7$ samples, only for the Mn-doped compositions even with low Mn concentration (x~0.1). However, neutron diffraction indicates that the ferromagnetic enhancement is of short-range order.

We have investigated further the origin of the enhanced ferromagnetic contributions on the basis of the Mn and Ru local electronic and magnetic structures, respectively, using X-ray absorption spectroscopy (XAS) and X-ray circular magnetic dichroism (XMCD) techniques. For $Ca_3Mn_{2-x}Ru_xO_7$, Ru^{4+} and Mn^{4+} valence states are concluded along the whole series, discarding the charge transfer from Ru to Mn. The observed ferromagnetic enhancement is then related to an intrinsic canting of the antiferromagnetically ordered Mn^{4+} spins, favored by Ru doping. In $Sr_{3-x}La_xSn_{2-x}Mn_xO_7$, the results confirm the presence of mostly Mn^{3+} cations suggesting a ferromagnetic vibronic-superexchange mechanism for these R-P phases, reminiscent of the ferromagnetism described in simple perovskites when Mn^{3+} is diluted with nonmagnetic ions [5] though in these layered compounds, long range ordered is not achieved.

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EXPLORING CARBON NITRIDE PROPERTIES FOR ELECTRODE IN AQUEOUS SUPERCAPACITORs

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Keywords: *Carbon nitride (g-C_3N_4), Energy storage, Supercapacitor, Capacitance.*

AMatS2.- Materials for Energy.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES

Rising energy demands require innovative solutions for efficient energy storage. Nowadays, energy investment is based on renewable energy. However, these current technologies have some drawbacks such as the potential energy production and the storage of energy.[1] The need to improve electric energy storage devices (EESs) has recently gained attention. Electrochemical double-layer capacitors (EDLCs) have emerged as promising candidates, requiring high surface area materials for optimal performance. We focused on the production of graphitic carbon nitride (g-C_3N_4) as an active material for EDLC electrodes, exploring various synthetic parameters (precursors, pretreatments, and heating rates) and exfoliation techniques such as acid, thermal, ball milling, and microwave treatment with the aim of enhancing surface area. As a precursor, melamine, dicyandiamide, and urea have been used. Dissolution and milling precursor pretreatment have been tested and four different heating rates (1, 5, 10, 15ºC/min) have been studied.[2] This comprehensive approach aimed to improve the g-C_3N_4 understanding and the electrochemical behavior in aqueous supercapacitor electrodes.[3] Structural and behavioral analyses employing diverse characterization methods are conducted to unravel the intricacies of g-C_3N_4 in supercapacitors. Ultimately, the most effective synthesis consisted in using melamine as precursor, without precursor pretreatment, and a heating rate of 15 ºC/min. Thermal exfoliation led to the highest increased surface area, and hydrochloric acid led to the highest capacitance.

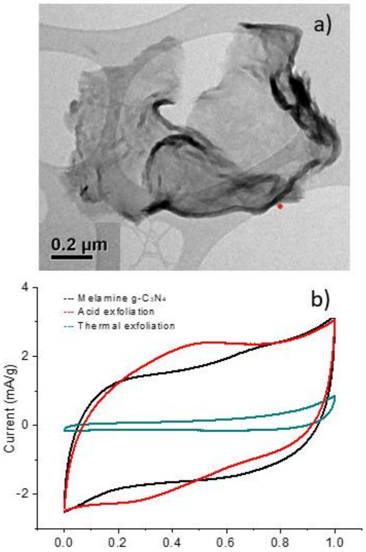

Figure 1. a) TEM image and b) CV of g-C_3N_4 synthesized at 15ºC/min from no pretreated melamine and exfoliated samples by acid and thermal methods.

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Oriented attachment one-pot synthesis of colloidally stable perovskite nanocrystals

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Keywords: *Perovskites, ultrasonication, oriented attachment, colloidally stable, semiconductors*

AMatS2.- Materials for Energy.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES

Colloidally stable semiconductors are in high demand today, and lead halide perovskites have emerged as a promising candidate. This study presents a straightforward method for synthesizing colloidally stable perovskite nanocrystals (NCs) with controlled morphology and optical properties.

We use ultrasonication via a tip-sonicator to transform cubic perovskite structures into nanowires through oriented attachment [1]. By adjusting the reaction time and temperature, we achieved tunable nanowire sizes, dependent on the initial cubic structure. Transmission electron microscopy confirmed the morphological transition from cubes to nanowires (NWs). Furthermore, we observed changes in emission and absorption spectra, reflecting the impact of morphological transformation on the optical behavior of the NWs. This rapid and versatile synthesis method holds promise for tailored lead halide perovskite nanowires, suitable for applications in optoelectronics and nanotechnology.

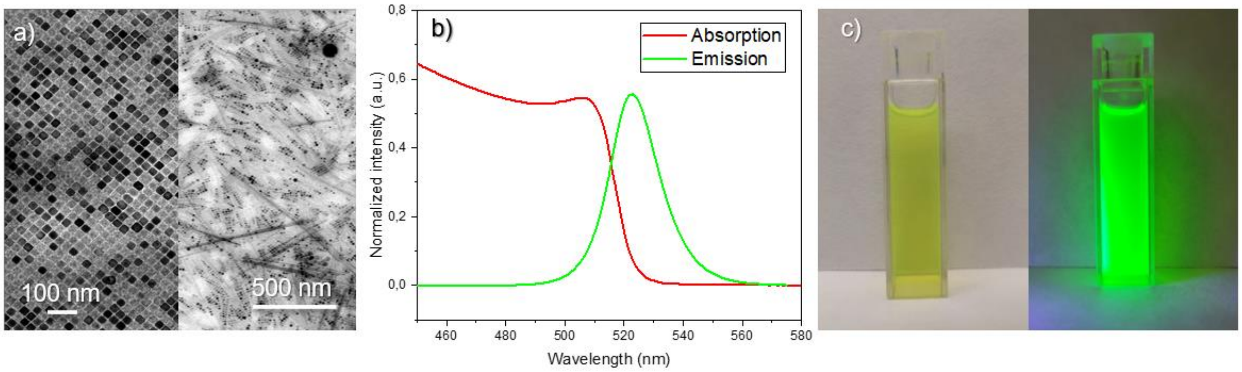

Figure 1: a) TEM image of the cubic perovskite nanocrystals and nanowires; b) Emission and absorption spectra; c) Colloidally stable perovskite solution under ambient light and under UV-lamp for comparison.

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PERYLENEDIIMIDES WITH CARBOXYLIC ACIDS IN THE IMIDE POSITION FOR ENERGY CONVERSION

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Keywords: *Perylenediimide, Perovskite Solar Cells, Quantum Dots*

AMatS2.- Materials for Energy.

Perylenediimides (PDIs) are a very important family of dyes constituted by two fused naphthalene units. Their aromatic core can be functionalized in the *bay* and/or *ortho* positions, thus allowing the control of the optoelectronic properties of the PDI as a function of the nature of the introduced groups [1]. Also, the *N*-imide positions are easily functionalized with primary amines. Due to this synthetic versatility, PDIs can be applied in different fields, being material chemistry one of the most important ones [2,3].

Here, we will present the synthesis of symmetric (PDI-1 and -2) and asymmetric (PDI-3 and -4) chloro bay-substituted PDIs, functionalized with different carboxylic acids in the imide positions (Figure 1). The latter groups allow the anchoring of self-assembled monolayers (SAM) in perovskite solar cells to create a new material for energy conversion. This study is carried on in collaboration with Prof. Antonio Abate at Helmholtz-Zentrum Berlin (HZB, Berlín, R.F.A.). On the other hand, the carboxylic units also allow the anchoring of PDIs onto the surface of quantum dots, synthesizing in this way a new hybrid material that can give rise to interesting energy transfer processes. In fact, the study of these new materials is performed in collaboration with Prof. Julia Pérez Prieto at the Instituto de Ciencia Molecular (ICMol, Valencia, Spain).

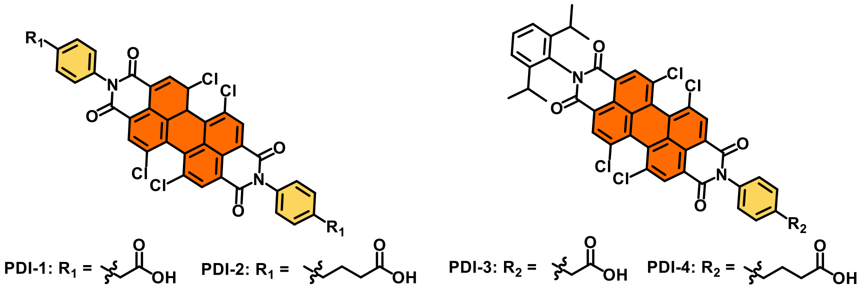

Figure 1 – Structure of the different PDIs synthetized

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Uncovering transport dynamics in metal halide perovskites

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Keywords: *Metal halide perovskites, microscopy*

AMatS2.- Materials for Energy.

Due to their remarkable properties, metal halide perovskites hold immense potential for energy transport and collecting applications. The understanding of charge carrier dynamics and recombination processes is paramount for harnessing their full potential.

Our research is based around sub-diffraction limited resolution diffusion measurements, coupled with spatially resolved spectroscopy. This combination of techniques forms a powerful synergy, offering a unique perspective into the fundamental parameters governing the behavior of charge carriers within these materials. [1] Our approach gives us unprecedented levels of insight on how carrier movement happens in metal halide perovskite.

Here I will present our latest developments for further improvement of this technique and the most recent results on energy transport in layered perovskites.

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ELEVATOR PITCH

LA3

A Biomimetic Follicle-Based Design for Engineering Reproductive Technologies

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Keywords: *bilayer hydrogel, oocyte, 3D cell culture, 3D printer, assisted reproductive technology*

AMatS3.- Smart materials with advanced functionalities.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES

In the field of assisted reproductive technologies, oocyte in vitro maturation (IVM) is emerging as a promising solution to overcome the limitations associated with traditional methods of stimulating the ovaries. Nevertheless, current IVM protocols suffer from a lack of standardization, often yielding lower-quality oocytes compared to those naturally matured in the female body [1]. To tackle this challenge, innovative biomaterials, specifically hydrogels, provide unique benefits in cell culture. They offer a three-dimensional cellular environment and allow for easy adjustment and characterization of mechanical properties, such as rigidity [2]. In this context, an inventive and reusable bilayer hydrogel system has been introduced to faithfully replicate the mechanical properties of the microenvironment surrounding oocyte maturation. This innovative system consists of an outer layer created from either a 3D-printed synthetic polymer (2-vinyl-4,6-diamino-1,3,5-triazine) or a natural polymer (chitosan), paired with an inner layer composed of alginate. By accurately mimicking the mechanical attributes of native tissue within a 3D culture environment, this system significantly enhances the quality and developmental potential of oocytes, ultimately leading to successful embryo development (Figure 1). It represents a notable advancement in assisted reproductive technologies by addressing the issues of non-standardized IVM protocols and the production of lower-quality oocytes. This innovation holds the potential to transform the field and enhance the outcomes of assisted reproductive procedures.

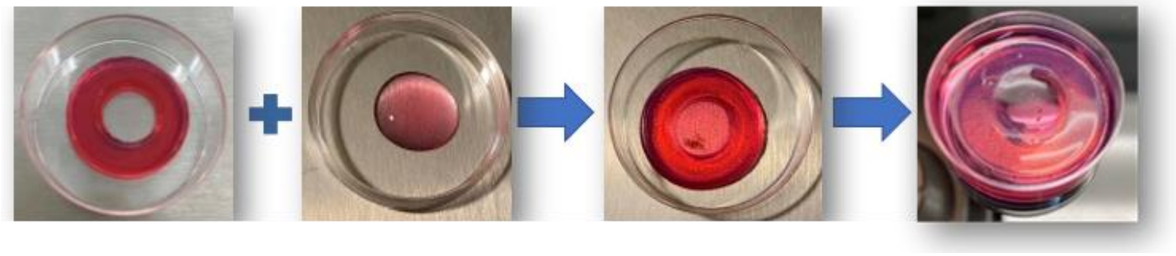

Figure 1: Bilayer hydrogel system in culture medium.

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ACOUSTIC METAMATERIAL BASED ON HELMHOLTZ RESONATORS FOR BROADBAND ABSORPTION

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Keywords: *Acoustic metamaterials, Helmholtz resonators, Acoustic absorption, sub-wavelength dimension.*

Indicate one of the following areas:

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES

New forms of mobility are demanding new material performances that standard materials have not got. A complete revolution in terms of acoustics and vibrations is expected in the transportation industry which is constantly searching for new acoustic treatments. Nowadays there are acoustic treatments on the market that act efficiently in the high frequency range, however new solutions are also required in the low frequency range. New artificial materials designed to control the transmission of waves, called acoustic metamaterials, has been a hot topic in the field of acoustics for several years. The design of these metamaterials is usually carried out by overlapping different wave control mechanisms. An example of this trend is the so-called Locally Helmholtz Resonators. These metamaterials are formed by sets of Helmholtz resonators coupled to a waveguide. This type of metamaterials is based on generating slow sound conditions so that the peaks of maximum absorption, corresponding to the resonance frequency of the Helmholtz resonators, suffer a drastic drop in frequency, allowing materials to be obtained with thicknesses of the order of sub- study wavelength. Slow sound conditions occur due to a change in sign in the real part of the effective compressibility modulus of the medium (at this point the speed of sound and wave number are pure imaginary, so there is no transmission of sound). This mechanism generates forbidden propagation bands at the resonance frequency of the resonators, so at frequencies lower than the resonance frequency of the Helmholtz resonators, dispersive sound conditions are generated that allow the speed of sound to be lower than in air and the dimensions of the metamaterial are smaller than the wavelength corresponding to the lowest frequency to be treated. Furthermore, by varying the dimensions of the assembly, the aim is to match the energy leaks with the intrinsic losses of the structure to achieve the critical coupling phenomenon and maximize absorption.

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AMatS
2ND CONFERENCE ON
ADVANCED MATERIALS IN SPAIN
NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

Cost Effective Flexible Surfaces for SERS based Detection

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Keywords: *Surface Enhanced Raman spectroscopy, Nanoimprinting, Sputtering, thermoplastics*

SERS is based on the enormous enhancement of the Raman signal of molecules adsorbed on suitable metallic nanostructures. As an analytical Raman scattering technique, SERS allows the identification of target molecules in complex mixtures based on their unique molecular vibrational fingerprint in a non-destructive and multiplexed manner [1]. The development of reliable methodologies for the preparation of homogeneous, robust and cost effective metallic nanostructure–based SERS substrates still remains a field of major interest [2]. This work aims to explore nanoimprint lithograhy (NIL) and sputtering techiques for the fabrication of uniform SERS active surfaces on transparent poly (methyl methacrylate) PMMA foils. In particular, moth-eye inspired features [3,4] coated with different thicknesses of metals (Au, Ag, Cu,Ta) are being studied to gain insight on the effect on plasmonic sensing (see Figure 1.a; 1.b). Such highly scalable approach allows a fine tuning of the optical response (see FDTD simulations in Figure 1.c) while ensuring a spatial uniformity of SERS response with high AEF in the order of 10^5 with a %RSD of 12% (Figure 1.d).

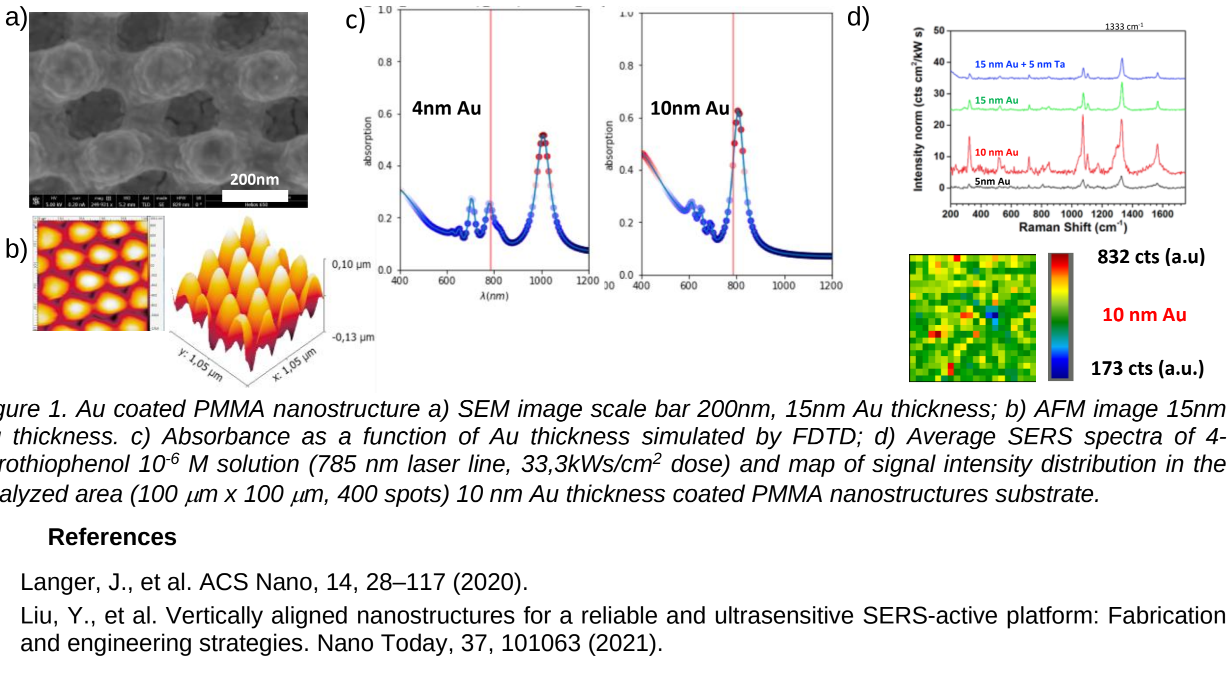

Figure 1. Au coated PMMA nanostructure a) SEM image scale bar 200nm, 15nm Au thickness; b) AFM image 15nm Au thickness. c) Absorbance as a function of Au thickness simulated by FDTD; d) Average SERS spectra of 4-nitrothiophenol 10^{-6} M solution (785 nm laser line, 33,3kWs/cm^2 dose) and map of signal intensity distribution in the analyzed area (100 μm x 100 μm, 400 spots) 10 nm Au thickness coated PMMA nanostructures substrate.

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DI-BLOCK *BENT-CORE* AMPHIPHILES AS NEW STRUCTURAL UNITS TOWARDS THE DEVELOPMENT OF FUNCTIONAL SUPRAMOLECULAR MATERIALS

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Keywords: *Supramolecular materials, bent-core liquid crystals, amphiphilic molecules, ionic conductivity.*

Indicate one of the following areas: AMatS3.- Smart materials with advanced functionalities.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: **YES**/NO

Bent-core liquid crystals (BCLC) [1] have emerged as highly innovative structures for a new generation of advanced supramolecular materials due to their unique properties (supramolecular chirality, ferroelectricity, and nonlinear optical activity among others, from achiral molecules). Especially in recent years, the use of amphiphilic *bent-core* compounds has led to the development of a wide range of supramolecular (thermotropic and lyotropic liquid crystals, nanoaggregates, and gels) and functional materials (chirality, ion conduction, etc...) [2] of technological interest.

Herein, the design, synthesis, and characterization (NMR, FTIR...) of novel di-block *bent-core* amphiphiles (composed of a hydrophilic unit uncoupled from a hydrophobic *bent-core* structure, bearing three different linkers X: -COO-, —, -N=N-), as well as their lithium and sodium complexes were carried out. In addition, materials characterization (POM, DSC, TGA, XRD) and structural-property studies were performed to assess their potential as functional supramolecular materials (e.g., *bent-core* liquid crystal electrolytes) (Figure 1).

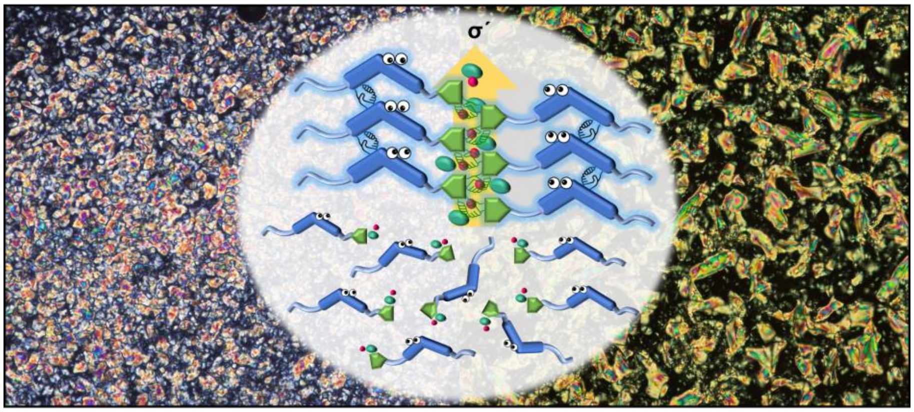

Figure 1. Supramolecular functional materials based on di-block bent-core amphiphiles.

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Flexible Piezoelectric Nanogenerator Based on MXene-coated Electrospun PVDF Nanofibers

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Keywords: piezoelectric *nanofiber, MXene, electrospinning, flexible sensor, energy harvesting*

At present, there is significant research attention directed towards portable, lightweight, shock-resistant, and cost-effective wearable devices that can ideally be powered by harnessing abundant mechanical or vibration energy. PVDF is one of the most frequently used piezoelectric polymers due to its high durability and reasonable piezoelectric coefficient values. However, their piezoelectricity strongly depends on their crystalline phase. Among the different phases such as α, β, and γ, the β-phase is considered as the electroactive phase and is crucial for piezoelectricity [1].

Recently, a new family of 2D materials with unique properties, known as MXenes, has been discovered. Its excellent properties include high electrical conductivity, mobility, and tunable structure, make MXenes suitable materials for flexible devices[2].

In this study, a piezoelectric nanogenerator (PENG) based on PVDF-TrFE copolymer mat obtained by electrospinning process has been developed and characterized. In order to enhance the piezoelectric performance of these nanofibrous structure, different contents of $Ti_3C_2T_x$-MXene in very thin film form was integrated onto the top and bottom surfaces of the electrospun PVDF-TrFE mats by a dip-coating procedure. The addition of MXene thin films improved the electrical conductivity of nanogenerator.

Crystallinity, morphology and piezoelectric performance of the MXene/PVDF-TrFE nanogenerator were explored in detail. The influence of the applied stress on the output of nanogenerator was also studied. The excellent piezoelectric performances of MXene/PVDF-TrFE make them of great potential for self-powered, wearable/portable devices.

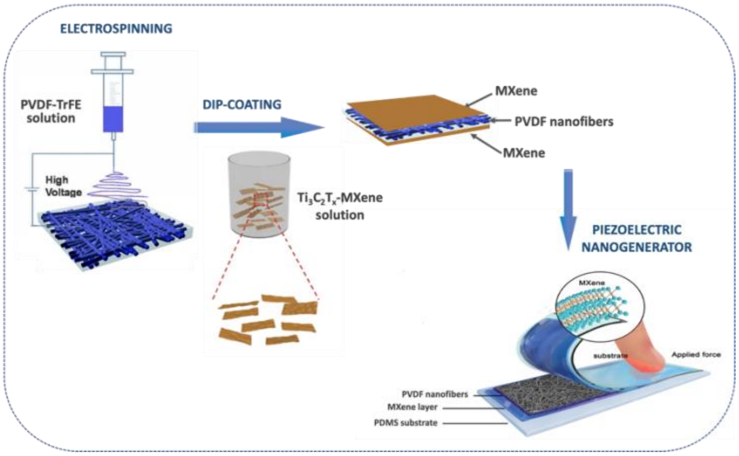

Figure 1 – Schematic representation of piezoelectric nanogenerator based on MXene/PVDF-TrFE

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MATERIALS INNOVATIONS FOR NEW GENERATION OF OFFSHORE TURBINE BLADES - ADHESIVES WITH INDUCTION HEATING FUNCTIONALITY

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Keywords: structural *adhesives, induction heating, magnetic nanoparticles, wind turbine blades.*

By 2050, the EU aims for the reduction of greenhouse emissions by transforming and redesigning the energy systems that account more than 75% of the EU emissions[1]. Offshore energy harvesting is key for achieving this as higher speed wind speed take place above the ocean that can lead to increased energy output[2]. The implementation of a large-scale and more efficient offshore grid will contribute to reach the targets set by the EU and to achieve 350 GW of offshore wind energy capacity[3]. However, the challenges that lie ahead are numerous, being some of them: i) the reliability and durability of the turbine blades (with the length of the blades continuously increasing, more severe structural requirements appear[4]); ii) the high costs, linked with the complexity in manufacturing, transportation, and installation of these components; and iii) their End-of-Life (EoL) management. All these aspects are widely related to the use of adhesives, since bonding is a key technology within blades manufacturing.

In this sense, one of the technologies being investigated by ITAINNOVA in the Carbo4Power project is related with the introduction of induction heating capacity in structural adhesives. This capability can be exploited in two directions: to produce a local heating in the bonded joints that can activate debonding-on-demand processes (another development being addressed in the project as a facilitator of the blade reuse/recycling); and to accelerate the curing reaction of the adhesives during manufacturing. The heating capacity is achieved in this case through the introduction of magnetic nanoparticles (MNPs) in the adhesive mass prior to bonding. This work presents part of the study carried out for this development. Different type of MNPs have been considered. The analysis done covers the evaluation of i) the mixing procedure, being critical in this case due to the higher tendency of these fillers to agglomeration issues; ii) the dispersions, through different micrographic techniques, iii) and the induction heating capacity introduced, depending on the particles concentration. From this investigation, a specific type of particles was selected.

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METAL-ORGANIC FRAMEWORKS IN NANOMEDICINE: DNA GRAFTING AS A METHODOLOGY FOR BUILDING COLLOIDAL & STRUCTURAL STABILITY IN BIORELEVANT MEDIA.

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Keywords: *MOFs, UiO66, DNA-grafted nanomaterials, colloidal stability*

Metal-organic frameworks (MOFs) constitute outstanding candidates among nanocarriers in medical imaging applications, due to their unique properties, including ultra-high surface area, permanent porosity, multifunctionality and facility in chemical modification. [1] However, MOF nanoparticles tend to decompose and aggregate rapidly in biological fluids, due to the presence of ionic species acting as competitors to the framework structure. [2] Post-synthetic functionalisation of the MOFs' surface with functional ligands, such as DNA oligonucleotides, is a promising option to prohibit unwanted interactions with the surrounding microenvironment and stabilize the nanoparticles. [1] In this present work, UiO66 was selected as an archetypal MOF to investigate the effect of DNA grafting on nanoparticle stability. UiO66 NPs were synthesised via the established solvothermal method, while DNA strands were self-assembled on UiO66 NPs' surface by metal-phosphate coordination bonding in a "salt-aging" process. We investigated the effect of DNA sequence composition (i.e., A_{30}, T_{30}, $(CCT)_{10}$, $(GGT)_{10}$) on nanoparticle stability by UV-Vis spectroscopy and Dynamic Light Scattering. Also, duplex-gated NPs were synthesised by hybridising the ssDNA-functionalized NPs with their complementary sequence. The duplex formation on UiO66 surface was identified by fluorescent indicator displacement and UV-melting assays. To evaluate colloidal stability, hydrodynamic size of all materials was monitored by time in a biological buffer. UiO66 NPs aggregated rapidly in the presence of phosphate ions and sedimented from the dispersant, while DNA motifs successfully reduced the aggregation rate according to the following order: $(CCT)_{10}<GC_{Duplex}<AT_{Duplex}<(GGT)_{10}<T_{30}<A_{30}<<$Bare UiO66 NPs. Currently, we are fully characterising the novel systems by complementary techniques such as TEM, XRD, TGA, as well as internalization assays in cancer cell lines.

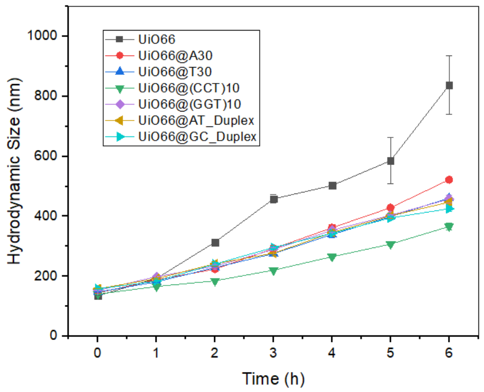

Figure 1 – Aggregation kinetics in PBS.

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PRECISION ENGINEERING OF CROSSLINKED SELF-ASSEMBLED STAR-SHAPED POLYPEPTIDE-BASED NANOMEDICINES

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Keywords: *Polypeptides, neurodegenerative diseases, PGA, nanomedicines, microfluidics,*

Polypeptides are already playing a major role on a number of different relevant areas such as nanomedicine.[1] Indeed, polypeptide-based nanomedicines allow architectural modifications and the introduction of bioresponsive elements that enhances drug(s) solubility, plasma stability, improves site-specific delivery, and controls drug(s) release kinetics.[1,2] In our group, by means of the implementation of controlled NCA polymerization techniques, followed by a bottom-up strategy, we have been able to obtain supramolecular nanostructures with interesting properties at the bio-nano interface. These nanoconstructs are based on self-assembled star-based polypeptide architectures using an “ordinary-extraordinary” transition behavior. [2,3]

To move a step further, herein we have modified our starting material (3-arm star-shaped polyglutamates (st-PGA)) with Taurine moieties, looking at the design of nanocarriers with a mainchain presenting intrinsic therapeutic properties, as Taurine has a key role in several human pathologies.[4] Moreover, we have explored the robustness and batch to batch reproducibility for our synthetic approach taking into account the needs for the scale up production of these nanotherapeutics to reach clinical development. This aim requires the implementation of flow chemistry, which support batch-to-batch reproducibility and cost-efficient processes. [5] We optimized microfluidic flow parameters to support the precision engineering of crosslinked compounds through two different in-flow crosslinking strategies: (i) biodegradable, using redox-responsive (disulfide) linkers, and (ii) non-biodegradable, a copper-free click reaction involving tetrazine-based ligation.[6] We used various microfluidic devices, which differ regarding herringbone and T-injection mixers, and obtained various nanomedicines shapes and sizes depending on the device. We exhaustively characterized our crosslinked taurine-derive polypeptidic materials using techniques such as ^{1}H-NMR, DLS, CD, TEM, and SAXS and studied their stability under physiological conditions. The biological evaluation of these nanoconstructs in relevant preclinical models is ongoing but the preliminary data obtained shows promising results.

Acknowledgments: This work has been supported by European Research Council (ERC-PoC-PolyBraint), the Spanish Ministry of Science and Innovation (PID2019-108806RB-I00 and FPI PRE2020-093092), Pol@Mats (MFA/2022/065). Part of the equipment employed in this work has been funded by GVA and co-financed with FEDER funds (PO FEDER of CV 2014–2020).

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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL PROPERTIES OF TITANIUM PHOSPHATE NANOFIBERS WITH INCORPORATED SILVER NANOPARTICLES

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Keywords: Titanium phosphate nanoparticle, silver nanoparticles, antibacterial properties.

AMatS3.- Smart materials with advanced functionalities (TICs, Biomaterials, Mobility, Habitat and environment)

Nanofibres are attracted a lot of attention in the last two decades because of their unique and appealing properties for use in different areas of medicine. Usually, different polymers as matrix nanofibers are easily fabricated of any type and shape. These nanofibres generally to be at disadvantage harsh conditions such as high temperature, irradiation, scratching, erosive solvents, etc. A good alternative could be titanium phosphate (*TiP*) materials are chemically stable with excellent ion exchange properties for easy incorporation of various agents, e.g. antibacterial compounds or drugs.

In the present study, we focused to incorporation of silver nanoparticles (*AgNPs*) into titanium phosphate nanofibers to obtain a nanosystem (*TiP@AgNPs*) for various antibacterial and biomedical applications. The TiP materials were obtained by MW-hydrothermal method at the various synthetic conditions. The effect of phosphoric acid concentration on the morphology of *TiP* materials were studied. It was found that the optimal conditions for obtaining *TiP* nanofibers ranged from 1.3 M to 2.5 M of H_3PO_4 at 180°C. The obtained TiP nanofibers were used for incorporation of antibacterial agents such as *AgNPs* at room temperature. The *AgNPs* were obtained during incorporation process by taking bulk Ag(I) salt. The obtained *AgNPs* are characterized a spherical shape with two different range sizes (*10* nm and *36* nm). In addition, the *TiP@AgNPs* nanosystems are showed a uniform distribution of *AgNPs* on the *TiP* surface based on TEM analysis (***Fig. 1***).

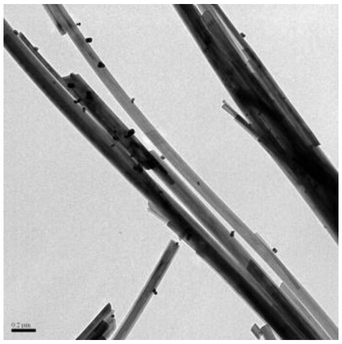

Figure 1 – TEM image of TiP@AgNPs

The results of antibacterial tests showed that *TiP@AgNPs* nanosystems have excellent antibacterial activity against gram-negative (*Escherichia coli*) and gram-positive (*Staphylococcus aureus*) bacteria. The *TiP@AgNPs* nanofibers are effective for prohibition of the growth of different bacteria and, therefore, are expected to be used as stable antibacterial materials.

Acknowledgements: This study was supported by CSIC program "UCRANIA DOCTORES 2022". The authors thank of the Spanish MINECO for MCI-21-PID2020-113558RB-C41 and PID2020-119130 GB-I00 grants.

POSTERS – LA1

2D materials as a playground for exotic exciton physics

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Keywords: *Excitons, Spin-orbit, Magnetism*

AMatS1.- Graphene and other 2D materials.

2D semiconducting materials exhibit fascinating properties such as large exciton binding energies and strong spin-orbit coupling, with potential use in spin physics and exciton-based devices. In particular, the monolayers BiI$_3$ and BiTeI are a good starting point for the study of exciton physics in unusual scenarios. On one side, the mechanical exfoliation of bulk BiI$_3$ to fabricate monolayers of BiI$_3$ should be possible as in the case of the paradigmatic 2D semiconductor monolayer MoS$_2$ [1], then expecting a 2D material with a really large exciton binding energy due to its particular stoichiometry. On the other side, monolayer BiTeI is a well-known semiconductor because of its large Rashba splitting [2]. The possibility of combining magnetic and non-magnetic 2D materials allows new heterostructures to emerge, manifesting exotic electronic and optical properties. In this context we perform a theoretical study of the excitonic properties of monolayer BiI$_3$ and heterobilayer BiTeI/MnI$_2$ with state-of-the-art first principles calculations, using the ab-initio GW+BSE scheme with a full spinorial formulation. In the case of the BiI$_3$ we find that the exciton binding energy is much higher than those of Transition Metal Dichalcogenide monolayers. The huge exciton binding energy suggests that this material is a good candidate as a material for exciton-based devices, as well as for the study of exciton dynamics. In the case of the bilayer BiTeI/MnI$_2$ a gap opens up compared to the monolayer BiTeI due to the presence of the magnetic interaction and it produces also a decrease of the Rashba parameter. The gap opening results in a splitting of the first bright exciton into two with opposite spin, with important consequences in the magnetooptical response. These results confirm the monolayer BiI$_3$ and the heterobilayer BiTeI/MnI$_2$ as promising candidates for the study of spintronics and as materials for exciton-based devices.

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2D nanomaterials in polymeric membranes for enhanced antifouling resistance. Application to water desalination.

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Keywords: *2D materials, nanoadsorbents, graphene oxide, membrane distillation, water purification*

Membrane distillation (MD) has emerged as a promising technology for water desalination purposes. This process is driven by a temperature difference between the hot salty feed water and the cold permeate side. The hydrophobic membrane that separates both water streams allows only water vapour molecules to pass through, while retaining all salts and non-volatile compounds (see Figure 1). As a result, high salt rejection rates (>99%) are typically achieved. Additionally, this technique has some great advantages over pressure-driven processes (e.g. osmosis processes):

- Production of ultra-pure water from highly concentrated feeds.
- Low electricity costs and potential implementation of removable energies: the majority of energy demand is related to feed heating, can be directly supplied by solar thermal energy or waste heat from power plants.
- Simplicity of equipment since high pressure is not required.

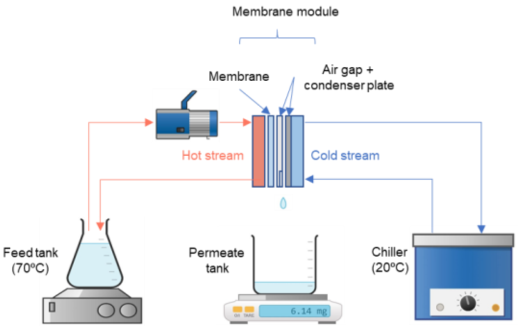

Fig. 1. Membrane distillation set-up. [1]

While MD offers several advantages, there remain challenges to address, primarily concerning the long-term stability of the membranes and its lower production capacity compared to reverse osmosis [2]. In particular, fouling is a main matter of concern as it is an unwanted phenomenon that causes deleterious performance, increases mass transfer resistance and leads to reduced quality and flux [3].

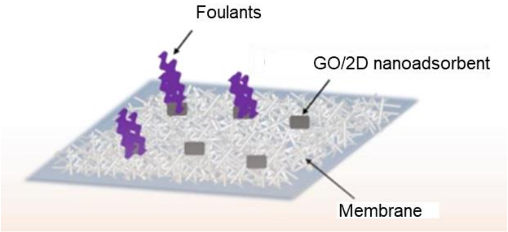

Fig. 2. Scheme of a modified membrane.

This work aims to synthesize membranes with enhanced fouling resistance and enlarged membrane lifespan. PVDF polymeric membranes have been loaded with graphene oxide (GO) dispersions to create sacrificial functionalized flakes that cover a small part of their surface in order to promote the deposition of foulants in them, protecting the remaining of the membrane surface (see Figure 2). MD has been carried out at 70 ºC in air-gap configuration. Preliminary results show that there is no flux reduction for optimum loadings on PVDF at salt rejections above 99.8%.

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Developing of Fe-Mg-Al catalysts for Hydrogen and CNTs production by Methane Cracking

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Keywords: *Carbon nanotubes, Fe-Mg-Al, Hydrogen, Methane.*

AMatS1.- Graphene and other 2D materials.

This work studies the catalytic cracking of methane (DCM) to obtain CO_x-free H_2, using Fe-Mg-Al catalysts. Selecting the optimum operating conditions, this process selectively allows to obtain different carbonaceous nanomaterials (CNMs), such as nanotubes (CNTs), nanofibers or even graphene, all of them with outstanding physical and chemical properties. To optimize this process, we have studied how the main operating variables affect the productivity of the catalyst and the quality of the CNMs [1].

Fe_xMgAl_2 ($0.1 < x < 1$) mixed oxides were synthesized following the citrates method, using a 2M dissolution of the metallic precursors (Fe, Al and Mg nitrates) and citric acid with 1:1 ratio (Met:Cit). The solution was heated to 90ºC in an oven for 12h and then was calcined at 800ºC during 3h, using a heating rate of 3ºC / min. The reaction was carried out at atmospheric pressure in a thermogravimetric system operated under differential conditions (i.e. low methane conversion). The operating conditions are: i) reduction stage: temp.: 775ºC, time: 1 h; total flowrate: 700 mL/min of H_2 / N_2 (50 / 50, % vol); ii) reaction stage: temp. range: 700-800ºC, time: 3 h; total flowrate: 700 mL/min of CH_4 / H_2 / N_2 (28.6 / 14.3 / 57.1, % vol).

The fresh catalysts were characterized by N_2 adsorption, XRD, TPR, Raman spectroscopy and SEM-EDX. For all the Fe loadings it formed a spinel structure after calcination. SEM-EDX analysis indicate that the atomic ratios (Fe/Mg/Al) agreed with the nominal composition. In addition, Raman and TPR results indicate that the degree of interaction of Fe Nanoparticles with the $MgAl_2O_4$ support strongly depend on the Fe content.

The maximum catalyst productivity after 3 h of reaction (32 gC/gcat.h) was obtained with the sample $FeMgAl_2$ at 775ºC. Higher reaction temperatures favour the encapsulation of Fe Nanoparticles, causing a severe catalyst deactivation. Regarding the type of CNMs formed, TEM images show that all the samples were selective towards the formation of CNTs. However, the quality of the CNTs, measured by the I_G/I_D ratio of the Raman spectra, increases with the reaction temperature, attaining the lower contents of structural defects at 800ºC. Therefore, the optimum temperature of operation (productivity and quality) is around 775–800ºC. The experimental kinetic results have been analysed using a model based on stages of the mechanism: adsorption of methane and carburization of Fe Nanoparticles, C atoms diffusion and precipitation, and deactivation of the catalyst [2].

Acknowledgements: The authors acknowledge the economic support of the EU, Horizon Europe RIA Programme, Grant nº 101069690 and to the MICIN-FEDER. STORMING project: PID1010-113809RB-C3.

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Generation of new lamellar phases and order alteration through soft exfoliation processes of MWW-type zeolites

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Keywords: *Lamellar zeolites, exfoliation, 2D materials*

AMatS1.- Graphene and other 2D materials.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: NO

Layered zeolites have traditionally been perceived as covalently bonded frameworks that extend across two dimensions. Simultaneously, the growth of crystals is confined in the third direction. The connectivity between these zeolite layers is achieved through hydrogen bonding, primarily involving silanol groups located on the surface of each layer, and potentially ionic or hydrogen bonding interactions with organic template molecules that are encased within the interlayer spaces.[1]

A 2-D layered zeolite precursor can be transformed to a 3-D zeolite (when the layers condense after removing the organic molecules present in the structure by calcination) or to a 2-D zeolite by the delamination or exfoliation of the individual zeolitic layers.

The process of delaminating layered zeolite precursors results in the formation of zeolites with a distinct advantage: it enables the entry of bulky molecules to access the catalytically active sites on the zeolite surface. Typically, these sites are limited to small molecules due to their location within microporous frameworks.[2]

In this work, we have found a procedure to transform the structure of the MCM-22(P) into a new layered zeolitic material, being also observed a partial disorder between MWW layers. That procedure consists of mixing the zeolite layered precursor with a surfactant like tetrabutylammonium fluoride and a metallic salt like zinc nitrate and applying a suitable temperature.

Later, the new material has been characterized using various techniques such as X-ray powder diffraction, nuclear magnetic resonance and elemental analysis. The structural modifications has been observed with transmission electron microscopy.

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GRAPHENE OXIDE ON THE IMPROVEMENT OF PROPERTIES IN CEMENT MORTARS

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Keywords: *graphene oxide, cement mortar, mechanical properties.*

AMatS1.- Graphene and other 2D materials.

Over the last few years, several studies in the construction sector have been focused on innovation with the aim of improving the properties of cement mortars to satisfy the demands of the market. In this direction, the use of graphene has raised interest in the construction industry due to its unique properties and versatility, with great potential to improve several characteristics and properties of traditional building materials [1]. The use of graphene oxide improves properties such as mechanical strength and durability, thanks to its ability to reinforce the matrix and prevent the formation of cracks [2], improve thermal and electrical conductivity, improve the barrier against humidity and corrosion [3], as well as fire resistance. For all these reasons, the present research work developed in the Department of Architectural Constructions of the University of Burgos, has focused on the study of the use of graphene oxide in cement mortars. For this purpose, different dosages with various percentages of graphene have been carried out, with the aim of optimizing the amount of graphene used, and its properties have been studied both in fresh and hardened state, trying to optimize the amount of graphene oxide used in cement mortars that provide this improvement of properties. Although graphene has great potential in the construction sector, its large-scale use still involves technical and economic challenges. Research and development of these materials helps to understand their behaviour in order to improve their integration as building materials with improved properties in the future.

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Acknowledgments

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Highly Anisotropic Bi_2S_3 for Polarization-Dependent Optoelectronic Device Applications

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Keywords: *Bi_2S_3, Anisotropic optoelectronic properties*

Deep physical insights into the highly anisotropic nature of Bi_2S_3 flakes, with D_{3d} point group symmetry, are obtained by employing polarization-dependent Raman spectroscopy and angle-dependent photoluminescence spectroscopy measurements. Altering the alignment of the system from parallel to perpendicular, with respect to the polarization of the incident laser, manifests itself as a considerable change in its Raman fingerprint for the respective orientations. Likewise, substantial signatures of its eminently anisotropic optoelectronic properties are seen upon investigation of the evolution of its angle-dependent photoluminescence spectrum, which reveals a photoluminescence dichroic ratio of ~2.3. Furthermore, the theoretical orbital-resolved electronic band structure of Bi_2S_3, calculated herein, strongly advocates its experimentally observed optoelectronic properties. Therefore, here, Bi_2S_3 is projected as a promising material for polarization-dependent optoelectronic device applications at room temperature.

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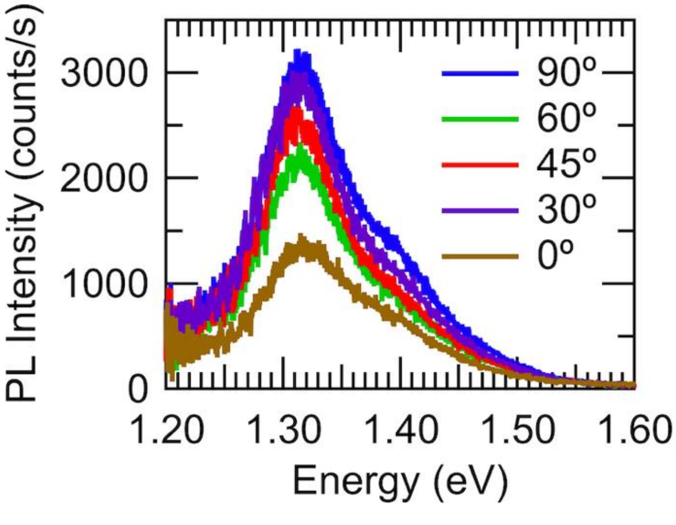

Figure 1: Angle-dependent photoluminescence spectra of a Bi_2S_3 flake

Imaging Adsorption Geometries of Organic Molecules on Metallic Surfaces by an Adaptive Tunnelling Current Feedback

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Keywords: *On-surface synthesis, Organic molecule, Atomic Force Microscopy (AFM)*

Atomic force microscopy (AFM) has become an essential tool for high-resolution imaging of fragile molecular entities adsorbed on a rigid substrate. Indeed, the surface influences the distribution and final configuration of these entities during adsorption; thus, fields such as biotechnology and molecular engineering make use of them to favour precise molecular arrangements and reactions and originate selectively new materials [1]. Specifically, the bond-imaging AFM technique, by using CO-functionalized qPlus sensors under ultrahigh vacuum and low-temperature conditions, can detect the backbone of organic molecules and monitor on-surface reactions for the synthesis of nanoribbons and 2D polymers from small precursors [2]. However, the proposed methods for determining the adsorption geometries of these molecules on a substrate remain complex and time-consuming. For the bond-imaging AFM technique, we have developed here a simple method that provides molecular/atomic resolution of molecules and surfaces together in a single image, which allows precise determination of molecular adsorption geometries. The method is based automatic feedback switch in the tunnelling current that, during scanning, adjusts the feedback parameters depending on whether the AFM tip is on an organic molecule or the substrate. The results on 2-iodotriphenylene (ITP) deposited on Ag(111) with atomic/molecular resolution in both materials prove the viability of the proposed method.

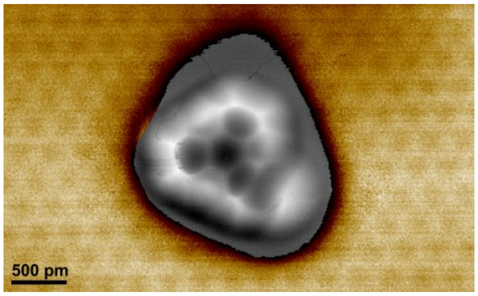

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Figure 1: - AFM image of ITP on Ag(111) taken with the adaptive tunnelling current feedback.

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Nanotubes of $(Sm_x,Y_{1-x})S$-TaS_2 based on quaternary Misfit Layered Compounds (MLCs)

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Keywords: misfit-layered compounds, electron microscopy, ((S)TEM), nanotubes
AMatS1.- Graphene and other 2D materials

Misfit layered compounds (MLCs) have garnered considerable attention due to their fascinating chemistry and properties [1]. MLCs consist of two different layered oxides or chalcogenides that are stacked alternately along their *c* direction. The MLC stack is composed of metal chalcogenide (MX) which is a distorted rock salt structure and a transition metal dichalcogenide (TX_2) which is a hexagonal structure[1,2]. The properties of MLCs can be tuned by the chemical and structural interplay between MX and TX_2. The nanotubes (NTs) from these MLCs offer potential applications in thermoelectrics due to the complementary properties of the two layered compounds [1]. Recently, a modified synthesis method of MLC-NTs has permitted the introduction of additional elements to form a quaternary compound starting from LaS-TaS_2 [3,4]. Here, we present an electron microscopy analysis of the novel family of (Sm,Y)S-TaS_2 nanostructures. In this novel family of MLS-NTs the partial exchange of Sm(S) by Y(S) provides a pathway for the fine control of the MLC structure and its properties.

TEM techniques including (high-resolution (scanning)TEM (HR(S)TEM) imaging, selected area electron diffraction (SAED) and energy-dispersive x-ray spectroscopy (EDS)) have been employed to profoundly analyse these nanotubes. HRSTEM and STEM-EDS allow the detailed investigation about the composition and atomic arrangement of these NT's. In Fig. 1: a, b, and c, three STEM images are presented, illustrating the repetitive layers of (Sm,Y)S and TaS_2. The study of the elemental composition of these NTs by EDS in Fig 1(d) reveals the atomic weight percentage of the Sm and Y in each batch $(Sm_x,Y_{1-x})S$-TaS_2. The results show that the substitution of Sm by Y is homogeneous and in-phase, with negligible effects on the material's lattice parameter.

In summary, through comprehensive Electron Microscopy analysis, we have demonstrated the successful synthesis of an unexplored group of quaternary MLC-nanomaterials.

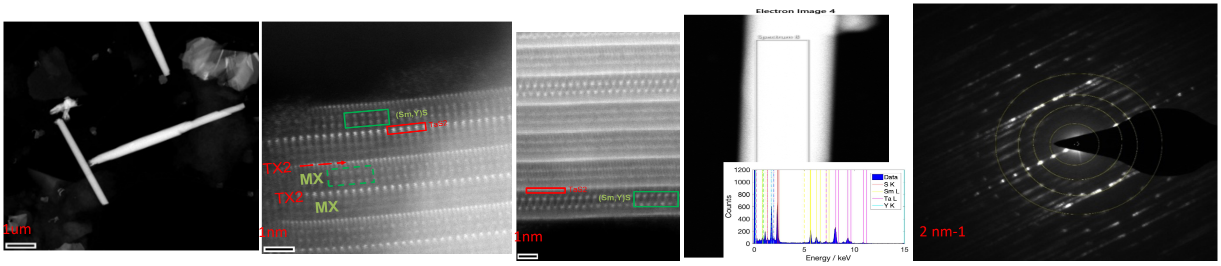

Figure 1: (a) 1 um and (b) 1 nm (c) 1 nm , STEM images of (Sm,Y)S-TaS_2 NTs with 20% percent of Y. (d) the EDS of a NT with similar percentage of Y. (e) SAED pattern of the NT.

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AMatS
2ND CONFERENCE ON
ADVANCED MATERIALS IN SPAIN
NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

Origin of discrete donor-acceptor pair transitions in 2D Ruddlesden-Popper perovskites

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Keywords: D*onor-acceptor pair, 2D Ruddlesden-Popper perovskites*

AMatS1.- Graphene and other 2D materials.

Two-dimensional (2D) van der Waals nanomaterials have attracted considerable attention for potential use in photonic and light-matter applications at the nanoscale. Thanks to their excitonic properties, 2D perovskites are also promising active materials to be included in devices working at room temperature **[1]**. Nevertheless, strong excitonic effects can reduce the photocurrent characteristics when using thinner perovskites phases **[2]**. In this work **[3],** we study the presence of very narrow and spatially localised optical transitions in 2D Lead Halide Perovskites by micro-photoluminescence and time-decay measurements. These discrete optical transitions are characterized by sub meV linewidths (≃ 120μeV) and long decay times (5-8 ns). X-Ray Photoemission and DFT calculations have been employed to investigate the chemical origin of electronic states responsible of these transitions. The association of Phenethylammonium with Methylammonium cations into 2D Ruddlesden-Popper perovskites, $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$, particularly in phases with n n ≥ 2, has been identified as a mechanism of donor-acceptor pair (DAP) formation, corresponding to the displacement of lead atoms and their replacement by methylammonium. Ionized DAP recombination is identified as the most likely physical source of the observed discrete optical emission lines. The analysis of the experimental data with a simple model which evaluates the coulombic interaction between ionized acceptors and donors returns a donor bohr radius of the order of ≃ 10 nm. This study opens new routes for optimization and development of future outstanding quantum and optoelectronic devices based on 2D Lead Halide Perovskites by means of DAP compositional engineering.

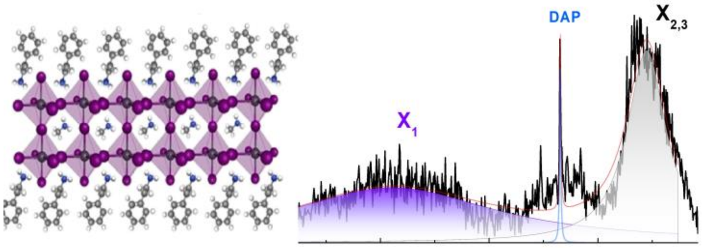

Figure 1 – Crystal structure of a monolayer of 2D perovskite, Donor Acceptor Pair (DAP) optical emission.

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AMatS

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ADVANCED MATERIALS IN SPAIN

NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

PHOTOEMISSION STUDY ON STABILITY OF TWO-DIMENSIONAL PEROVSKITES SINGLE CRYSTALS FOR OPTOELECTRONIC APPLICATIONS

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Keywords: *Two-dimensional perovskites, Stability, Degradation, Surface oxidation, Photoluminescence spectroscopy, Photoemission spectroscopy.*

AMatS1.- Graphene and other 2D materials.

Abstract: 2D halide perovskites hold a great promise for electronics and optoelectronics applications due to the structural diversity, high absorption and photoluminescence, and tunable bandgap. Especially, they are one of the most promising studied material for photovoltaics. However critical issue is their low stability to ambient environment conditions. In this work, we have investigated degradation processes of 2D halide perovskites upon external factors such as oxygen, humidity, light, heat and photo-induced exposition. We have applied X-ray photoemission spectroscopy techniques, as well as optical techniques (micro-photoluminescence, micro-Raman spectroscopy), to demonstrate that 2D perovskites easy degrade upon heat and laser illumination in atmospheric conditions. Surprisingly, we have found a different aging chemical processes after crystal exposition to long periods (up to 1 year) in atmospheric conditions with and without the presence of external light. Crystals exposed to light aged into morphology with micro-holes and they are not photoluminescent active. On the other hand, crystals under dark conditions show wire-like morphology maintaining photoluminescence. The degradation processes finally results in removal of organic part from the crystal and formation of lead and iodine vacancies, which are probably related to side non-radiative recombination mechanisms responsible for the photoluminescence degradation. These vacancies are associated with crystal decomposition into PbI_2, metallic Pb, and Pb oxides. This work is benefical for development of long-term stable perovskite devices with an enhanced optical performance.

Predictive Modeling of 3D-Printability and Final Properties of Polymer Composites Incorporating 2D Materials

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Keywords: PLA, *2D-material, 3D-printing, rheology, data-driven* (AMatS1)

Three-dimensional (3D) printing of thermoplastic polymer nanocomposites incorporating 2-dimensional (2D) materials enables cost-effective production of complex structures with multifunctional properties. However, a diverse set of printing parameters (e.g., flow rate and extrusion temperature), material properties (e.g., thermal behavior and rheological properties), and the incorporation of 2D materials, since they alter rheological and thermal properties, greatly influence printability and the resultant performance of polymer nanocomposites incorporating 2D materials [1]. The main objective of this study is to develop a predictive model for the processing and property forecasting of 3D-printed multifunctional polymer composites while revealing the material-processability-property relationship. Two commercially available bio-based PLAs with high and low molecular weights and two different nanomaterials nanoclay (NC) and graphene nanoplatelets (GPN) were used to prepare nanocomposites in varying compositions (wt.% 0.5, 1, and 3). Since rheological and thermal properties have been shown to have a significant effect on printability and final quality [1,2], time sweep experiments were used to control the complex viscosity, storage modulus, and thermal stability of samples. For the printing and quality assessment, three cylindrical specimen samples of each composition were printed using a novel pellet printer. To investigate the effect of nozzle temperature and extrusion flow on the printability and final properties of samples, each composition was printed at varying temperatures and extrusion flows. Printing quality was assessed by measuring the weight of samples to determine over/under extrusion and by image processing to determine the variation of internal diameter and surface roughness. Storage modulus and thermal stability had a significant effect on over- and under-extrusion and geometrical properties. Increased storage modulus and decreased thermal stability resulted in under extrusion and made it impossible to print in extreme cases like high molecular PLA with 3 wt.% NC. As a next step, a predictive model will be developed to assess printability and predict the resultant properties using rheological properties as material indicators. The second purpose of this study is to use the design of experiments and a semi-automated system for composition optimization of PLA nanocomposites incorporated with three different 2D materials (NC, GNP, and boron nitride). Latin Hypercube Sampling (LHS) and Bayesian Optimization (BO) were employed to predict new compositions to improve the impact strength of the compositions, while custom-made dispenser and automated Charpy impact system were used to prepare predicted compositions, and measure impact strength, respectively.

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THE ALBA LEEM-PEEM FOR ADVANCED MATERIAL CHARACTERIZATION

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Keywords: *Characterization techniques, Nanospectroscopy, XAS/XPS, LEEM-PEEM*

AMatS1.- Graphene and other 2D materials.

AMatS2.- Materials for Energy.

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

ALBA is a third generation Synchrotron located close to Barcelona [1]. It offers users state of the art synchrotron radiation experiments through regular academic call for proposals or proprietary access and is currently expanding its services towards Electron Microscopy [2,3] and combined approaches including scanning probe techniques [3]. The LEEM-PEEM endstation of the soft x-ray CIRCE beamline offers a suite of surface characterization techniques for advanced materials based on PhotoEmission Electron Microscopy (PEEM) and Low Energy Electron Microscopy (LEEM) coupled to the spectroscopic power of a fully tuneable x-ray source (XAS,XPS, XMC(L)D) [4].

To illustrate the possibilities available to the user community, we will show examples of measurements performed on materials from different fields, addressing their structural (microspot LEED and darkfield imaging), chemical and electronical properties with a spatial resolution down to few tens of nanometers. The station also allows for in-situ sample preparation (evaporators, annealing, gases), UHV/argon sample transfer, and disposes of a range of dedicated sample holders for operando measurement (temperature, electric signals and magnetic fields, time resolved measurements) [5].

The authors acknowledge the support of all ALBA staff, in particularly from E. Pellegrin, S. Ferrer, S. Ruiz-Gomez, A. Mandziak, M.W. Khaliq, J. Prat, A. Martinez-Carbonero, L. Souza, F. Becheri, A. Camps, A. Fontsere, J. Alvarez, N. Gonzalez, J. Ferrer, D. Calderon, V. Massana, and many more.

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[2] JEMCA (Joint Electron Microscopy Center at ALBA)

[3] InSitu Correlative Facility for Advanced Energy Materials subproject of the ´Planes Complementarios con Comunidades Autónomas´ of the Recovery, Transformation and Resilience Plan - Funded by the European Union -Next Generation EU, in partnership with ICN2, ICMAB-CSIC and PIC-IFAE

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AMatS
2ND CONFERENCE ON
ADVANCED MATERIALS IN SPAIN
NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

THERMAL PROPERTIES ACROSS 2D-LAYERED MATERIALS

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Keywords: *2D-Materials, thermal properties, thermal management, acoustic properties*

This work presents a comprehensive overview of three interrelated scientific investigations that collectively address the engineering of thermal transport in two-dimensional (2D) materials. In these studies, various aspects of thermal management and control are explored. The first study demonstrates the successful engineering of ultra-thin lattice mismatched $Bi_2Se_3/MoSe_2$ superlattices and graphene/$PdSe_2$ heterostructures using molecular beam epitaxy.[1] The second study provides a comparative investigation of the impact of crystallinity and film thickness on the acoustic and thermal properties of layered $PtSe_2$ films. The research reveals the potential for tuning lattice thermal conductivity through crystallinity, demonstrating a reduction in thermal conductivity for polycrystalline films compared to their crystalline counterparts. Additionally, the study highlights the significance of optical phonons in thermal conductivity and uncovers strong interlayer interactions and acoustic phonon lifetimes. [2] In the third study, a systematic examination of in-plane and cross-plane thermal conductivity in crystalline $SnSe_2$ films with varying thickness is presented. The research uncovers a thickness-independent thermal conductivity anisotropy ratio and a consistent decrease in thermal conductivity with decreasing film thickness. Furthermore, the study identifies the contributions of phonons with different mean free paths to the overall thermal conductivity.[3] Collectively, these three studies offer a holistic perspective on the engineering of thermal transport in 2D materials. They provide crucial insights into synthesis, characterization, and thermal behaviour, ultimately contributing to the advancement of thermal management technologies and the development of tailored thermoelectric devices.

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Wednesday, November 15th - LA2

LA 2 Emma Kendrick:

Battery Sustainability; Materials and Design

We explore sustainability in relation to new battery technologies, focusing on sodium-ion batteries and their recycling potential. We consider the critical role of materials in the circular economy, emphasizing the need for alternatives to lithium, cobalt, and graphite. Sodium-ion batteries offer cost-effective substitutions but require attention to recyclability and carbon emissions. The study also addresses design considerations for disassembling sodium-ion batteries and proposes specific strategies for electrode manufacturing to enhance sustainability through efficient recycling and reuse.

AMatS
2ND CONFERENCE ON
ADVANCED MATERIALS IN SPAIN
NOVEMBER 13TH TO 15TH 2023 - ZARAGOZA (SPAIN)

Scaling-up of Solid Oxide Cells for the development of high temperature electrolysers

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Keywords: *Hydrogen, electrolysis, solid oxide cells, SOFC, SOEC.*

AMatS2.- Materials for Energy.

Green hydrogen is a versatile energy carrier that will play a fundamental role in achieving the decarbonisation objectives to which Europe has committed [1]. In particular, in the coming years it will be necessary to significantly reduce the cost of producing green hydrogen by electrolysis. Today, the technology is carried out at low temperature with alkaline or polymeric electrolysers [2]. Advantages of high temperature over conventional low temperature technologies include: lower consumption of electrical energy, lower cost of cells and auxiliary system components, higher current densities at lower operating voltages and efficiencies close to 100% [3].

The objective of this work is to develop planar Solid Oxide Cells (SOCs), supported on the hydrogen electrode, with a high large sizes (5x5cm^2) for further scaling up of high temperature electrolysers. The selected configuration of the cell is composed by Ni-yttria stabilized zirconia (Ni-YSZ) cermet as the H_2 electrode, yttria stabilized zirconia (YSZ) as the electrolyte and lanthanum strontium manganite- yttria stabilized zirconia (LSM-YSZ) as the O_2 electrode. The cell is supported in a highly porous layer (40% porosity) of ~350 µm thickness. Corn starch was employed as pore former. Between the porous support and the electrolyte, a functional layer of 50 µm thickness was added. Aqueous tape casting was chosen as the fabrication method for both the hydrogen electrode and the electrolyte. Finally, the O_2 electrode was depostied by screen printing. This manufacturing process allowed to obtain homogenous layers and very planar cells, taking advantage of the scalability of the methods, and therefore to have reproducible results.

Electrochemical performance of the cells will be presented and discussed. At 800 °C, Area Specific Resistance (ASR) values of about 0,6 Ωcm^2 were achieved. Current density values in fuel cell mode (SOFC) of about 0,8 Acm^{-2} at 0.5V and in electrolysis mode (SOEC) of about -1 Acm^{-2} at 1.3V were also measured. These results are comparable with state of the art cells provided by commercial suppliers such as Fiaxell and SOFCMAN. Durability studies are also being performed to assure the stability of the cells for long term operation under electrolysis mode. Preliminary results showed that the cells fabricated at INMA present better microstructural stability in comparison with the cells supplied by SOFCMAN, due to the microstructural optimization of the Ni-YSZ supports. We can conclude that the present cells are competitive with commercial ones and currently a first SOC prototype stack is under fabrication.

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TOWARD COST-EFFECTIVE MAGNESIUM BATTERIES: FROM OXIDES TO SULFUR AS CATHODE MATERIALS

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Keywords: *Mg batteries; $MgMn_2O_4$; Mg^{2+} insertion; cathode structure evolution; sulfur.*

AMatS2.- Materials for Energy.

Rechargeable Mg batteries constitute an alternative to their Li counterparts due to their enhanced safety features and reduced cost. Despite these advantages and several decades of research on Mg battery technology, their commercialization is still far from reality. One bottleneck is the difficulty of combining electrolytes and electrodes allowing for both reversible Mg insertion-extraction at high enough potentials and reversible Mg deposition-stripping. Among potentially cost-effective cathode materials we find both Mg oxides and sulfur. For instance, the spinel $MgMn_2O_4$ has been studied in this context. Although Mg^{2+} can be reversibly inserted in the $MgMn_2O_4$ structure leading to $Mg_2Mn_2O_4$ (Mn^{3+}/Mn^{2+}), the reversible extraction of Mg from $MgMn_2O_4$ is more attractive. The corresponding Mn^{4+}/Mn^{3+} redox process leads to a theoretical capacity of 272 mAh g^{-1}.

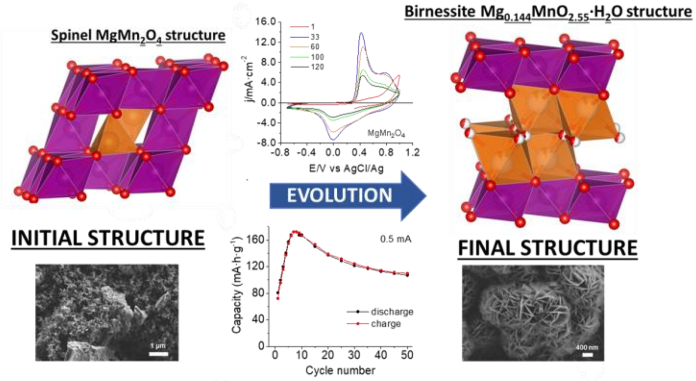

Figure 1 – Schematic illustration and TEM images of the structure evolution after repeated charge/discharge cycles.

$MgMn_2O_4$ featuring a tetragonal structure has been synthesized using the Pechini method and tested in aqueous media [1]. Electrochemical measurements combined with in-situ Raman spectroscopy and other characterization techniques show that the charge/discharge process occurs through the simultaneous co-intercalation of Mg^{2+} and water molecules. A progressive transformation from a well-defined spinel to a birnessite-type structure takes place during the first cycles and it provokes capacity activation. The concomitant towering morphological change induces poor cycling performance, probably due to partial delamination and loss of electrical contact between the active film and the substrate. This work emphasizes the key roles of the solvent molecules and the cathode restructuring in the Mg^{2+} insertion process and, in turn, in the applicability of cathode materials[1].

On the other hand, sulfur (or MgS) is an attractive candidate for cathode material. One of the main challenges for the design of a practical rechargeable Mg metal battery is finding an appropriate electrolyte, compatible with Mg deposition stripping on common substrates and showing a reversible sulfur redox process. Preliminary results obtained in our laboratory along these lines and prospects will be discussed. This study forms part of the Advanced Materials programme and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by Generalitat Valenciana.

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OPERANDO RAMAN SPECTROSCOPY FOR REDOX FLOW BATTERIES

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Keywords: *Raman spectroscopy, redox flow cells.*

AMatS2.- Materials for Energy.

Energy generation from renewable sources has become crucial to achieve decarbonization and the transition to a more sustainable energy production. The unpredictable and intermittent nature of renewable energy sources such as solar or wind power requires efficient and cost-effective energy storage systems (ESS) to match energy production and demand. Redox flow batteries (RFB) are especially suitable EES for large-scale stationary energy storage, with competitive advantages over conventional batteries including cost-effectiveness, long cycle life and independent scalability of energy and power. In particular, aqueous organic redox flow batteries (AORFBs) are gaining much interest, as they use more sustainable and abundant organic redox-active species than the state-of-the-art vanadium RFB. While many organic molecules exhibit promising key performance indicators, their cycle stability should be further improved for large-scale deployment of AORFB [1]. With several sources of capacity decay in AORFB, identifying involved processes is crucial to develop strategies to prevent or minimize capacity fading. This requires the development of advanced *in-situ* techniques to investigate capacity fading mechanisms of RFB in operando conditions.

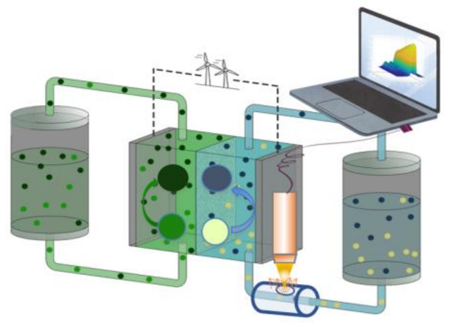

Figure 1-Scheme of the experimental setup

In this contribution, the implementation of Raman spectroscopy for in operando characterization of AORFBs will be presented. Raman spectroscopy is a powerful analytical technique that provides the chemical fingerprint of redox-active molecules. However, this technique has not been exploited in RFB despite its intrinsic advantage over more commonly used tools such as UV-Vis spectroscopy to investigate strongly coloured highly concentrated solutions. Overall, the aim of this contribution is to promote the use of Raman spectroscopy within the RFB community by disclosing technical details for implementation and illustrating its capabilities with some use cases. The tailored design and fabrication of a Raman flow cell for practical implementation of operando Raman spectroscopy for RFB characterization will be presented (Figure 1). Then, Raman spectroscopy will be applied to monitor the state-of-charge and explore degradation processes in the catholyte of ferrocyanide-based RFB. Importantly, the proposed methodology may be of interest for other research fields as it is implementable in other electrochemical flowing systems such as semi-solid flow batteries, electrochemical pollutant oxidation, electrosynthesis, electroanalysis, etc.

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NOVEL ELECTROLYTES FOR ALKALINE AND ALKALINE-EARTH METAL BATTERIES

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Keywords: *magnesium battery, lithium battery, sulfur cathode, ammoniate, borohydride, bismuth anode*

AMatS2.- Materials for Energy.

The development of alkaline and alkaline-earth metal batteries is limited by the lack of electrolytes with enough conductivity and low flammability that allow for reversible metal deposition-stripping. Such electrolytes should also have a wide enough potential window and sustain the cathode process and they should be cost-effective (based on non-critical raw materials). To meet these requirements, novel formulations that minimize or suppress the use of organic solvents are needed. Our emphasis is being put on solid electrolytes based on either polymers (polyethylene oxide or polyethyleneimine) or metal borohydrides that can be integrated in lithium-sulfur and magnesium-sulfur batteries.

In the case of the electrolytes based on metal borohydrides, the presence of either ammonia or amines in the final formulation has been found to be beneficial for enhancing conductivity of the solid electrolyte. The ammonia solvates of metal borohydrides (and other salts) are often referred to as ammoniates and they are frequently either liquid or solid electrolytes. In our laboratory, some ammoniates (mainly based on sodium and including that of borohydride) have been prepared and characterized, showing outstanding properties as electrolytes for sodium metal batteries [1,2].

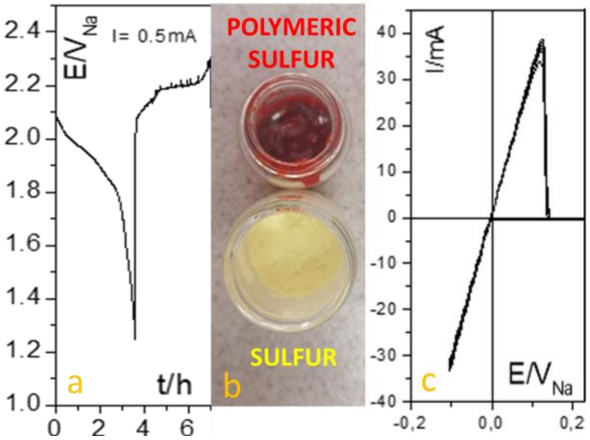

Figure 1 – a) Galvanostatic cycle for an ammoniate-based Na-S battery (poly-S shown in b)). c) CV for the Na process on Cu in $NaBH_4 \cdot 2.5NH_3$

The challenge of making compatible the ammoniates with sulfur cathodes will be discussed. Fig. 1(a) shows the first charge/discharge cycle for an ammoniate-based Na-S battery. While the result is promising the sulfur electrode has a poor cyclability, even in the case of employing the so-called polymeric sulfur in which the sulfur chains are interconnected by 1,3-diisopropenylbenzene units. In contrast, the excellent reversibility of the sodium process, not only for Na metal electrodes, but also for Cu substrates should be highlighted. Such a reversibility is also found when employing bismuth anodes, giving rise to intermetallic Na-Bi compounds. These anodes keep on having a high gravimetric capacity while reducing the risks due to the presence of Na metal, which increases their applicability. The prospects of extending these results to Li-S and Mg-S batteries based on liquid or solid ammoniates will be analyzed together with some preliminary results from our lab. This study forms part of the Advanced Materials programme and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by Generalitat Valenciana.

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Exploring Processing Effects on the Direct Recycling of $LiFePO_4$

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Keywords: $LiFePO_4$; recycling; valorisation; characterisation

AMatS2.- Materials for Energy.

To reduce global emissions and the associated adverse effects of climate change, the electrification of infrastructure is now being realized. With the green energy transition underway, it is important to have forward thinking towards a circular economy and mitigate a future crisis with respect to critical materials supply which are found in Li-ion batteries (lithium, cobalt, graphite, phosphorus)[1]. While there are many cell chemistries in use, this presentation will focus primarily on $LiFePO_4$ (LFP) – a commercial cathode chemistry widely used due to its inherent stability while cycling.

While attention has been given to other cell chemistries (such as layered lithium metal oxide materials: such as $LiCoO_2$ and $LiNi_xMn_yCo_zO_2$ where x+y+z=1) in the recycling sphere, LFP recycling is now gaining attention. While pyrometallurgy[2] and hydrometallurgy[3] are conventional routes for recycling, attention is shifting to direct recycling approaches which for LFP involves regeneration to relithiate. While there are multiple approaches involving either additional reagents[4] or thermal treatments (to remove the binder)[5], how these approaches affect the LFP material are limited.

Thus, in this presentation, initially an overview of current LFP (direct) recycling methods will be covered, before covering the characterisation techniques necessary to benchmark the health of the LFP material and provide a full quantitative elemental breakdown of cells which have limited information provided by the manufacturer. The presentation will then focus on evaluating material changes upon processing towards a direct recycling route to achieve a re-lithiated LFP for re-use.

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Enhanced gas separation performance (CO_2/CH_4) of thin film composite membrane based on Pebax and zeolitic imidazolate frameworks.

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Keywords: Zeolitic Imidazolate Frameworks (ZIFs), Pebax Renew®, Separation performance (CO_2/CH_4), Thin film composite (TFC) membrane.

Indicate one of the following areas: AMatS2.- Materials for Energy.

Gas separation technologies are critical for addressing environmental concerns and energy sustainability. This study investigates the impact of integrating Pebax Renew®, a sustainable polymer material, with zeolitic imidazolate frameworks (ZIFs) to develop advanced membranes for the selective separation of a 50/50 CO_2/CH_4 mixture. Pebax Renew®, known for its eco-friendly attributes and exceptional gas permeability, serves as the polymer matrix[1,2]. ZIFs, characterized by their tunable pore structures and high selectivity, are incorporated into the Pebax Renew® matrix to enhance gas separation performance. The fabrication process of ZIF/ Pebax Renew® thin films is optimized to achieve uniform and defect-free membranes. The gas separation performance of these composite membranes is comprehensively evaluated using a mixed gas feed of CO_2 and CH_4, replicating conditions encountered in carbon capture and natural gas processing. Crucial membrane properties, including permeability, selectivity, and separation efficiency, are rigorously analyzed with variations in ZIF type, loading levels, film thickness, and operating conditions. The results demonstrate that the incorporation of ZIFs into the Pebax Renew® matrix leads to a substantial enhancement in the membrane selectivity for CO_2 over CH_4, resulting in significantly improved separation efficiency. The influence of different ZIF compositions and concentrations on membrane performance is explored, highlighting the potential for tailoring the membrane to meet specific gas separation requirements[3]. Herein, this study highlights the potential of thin film composite membranes composed of Pebax Renew® and ZIFs as a sustainable and highly efficient solution for CO_2/CH_4 gas separation. These membranes are a promising material for reducing greenhouse gas emissions and enhancing the efficiency of natural gas processing, thereby addressing critical environmental and energy challenges. Further research into optimizing the membrane fabrication and scaling up production could lead to practical applications across various industrial processes, aligning with sustainability goals and energy demands.

Acknowledgment: We would like to extend our gratitude to GreenLifTech project (TED2021-130621B-C41) supported by the European Union-NextGenerationEU, Ministerio de Ciencia e Innovación/MCIN for the valuable support and funding in advancing this research. Their commitment to environmental sustainability and technological innovation has been contributed in driving this project forward. Grant T68-23R from the Aragon Government is also acknowledged.

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PIEZOELECTRIC PAINT AS ENERGY HARVESTER

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Keywords: *piezoelectric paint, energy harvester, vibration*

AMatS2.- Materials for Energy.

The aim of this study is to analyse the electrical power generated by piezoelectric paints that cover structures subjected to vibrations. The paint is a suspension of milled lead zirconate titanate (PZT) ceramic powder in a polymer binder (water-based acrylic) [1]. In addition, two electrodes are required to connect with the electrical load. When the structure covered by the paint vibrates, the mechanical vibration energy is harvested by the paint, transforming it in electrical energy. Figure 1 shows a schematic of the working principle. The piezoelectric paint can be modelled as a source voltage in series with a capacitor [2] as shown in Figure 2. The electric power depends on the electro-mechanical characteristics of the paint, its geometric dimensions, the frequency and amplitude of the vibration and the electrical load. In this study the electric power is anlysed as a function of the electrical load. The connection in series and parallel of two piezoelectric paint generators is also studied. Figures 3 and 4 show the results. The power is maximum for a specific electrical load. When the two paint generators are connected in series or parallel the electric power is doubled, but the peak value of the power is obtained when the electric load is doubled (series connection) or is half (parallel connection).

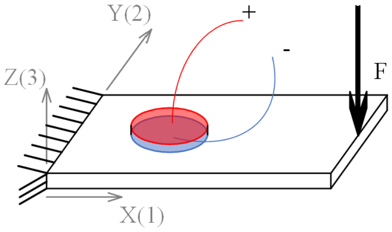

Figure 1 –Schematic of the working principle

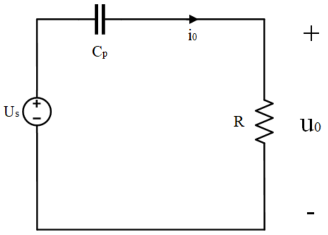

Figure 2 – Electric circuit equivalent model

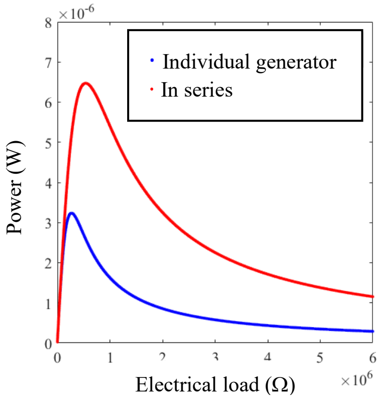

Figure 3 – Generators connected in series

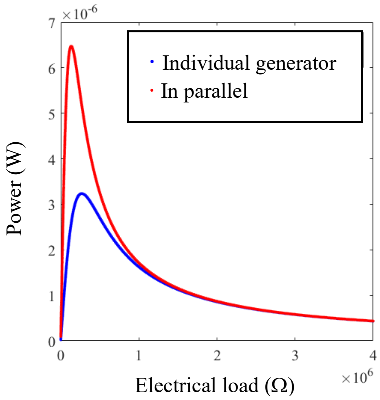

Figure 2 – Generators connected in parallel

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MULTISCALE SIMULATION FRAMEWORK IN THE DEVELOPMENT OF ADVANCED CONCRETE-BASED MATERIALS WITH AEROGEL ADDITIVES FOR FAÇADE PANELS IN NEARLY ZERO WASTE ENERGY BUILDINGS

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Keywords: multiscale simulation, Textile-Reinforced Concrete, Cellular Lightweight Concrete, aerogel, Zero Waste Energy Building

Abstract

The scarcity of natural resources and the increasing awareness of the need to reduce energy consumption have driven the adoption of principles such as "Zero Waste Energy Building" in the development of construction materials. In this context, lightweight and insulating materials like Cellular Lightweight Concrete (CLC) and aerogel, reinforced by other materials, such as Textile-Reinforced Concrete (TRC), represent a promising avenue to meet these objectives by enabling more efficient and sustainable structures [1].

The behavior of these composite materials is complex due to the interaction of several variables at different scales. Hence, for instance, in a wall façade panel of CLC with aerogel covered by TRC layers, the thickness of the aerogel structure is a few nanometers, while layer thickness and woven structure size are in millimeters. Due to this complex interrelationship, the configuration of this combination requires numerous experimental tests, which could be partially avoided by simulation-based design tools [2].

In this work [3], a multiscale methodology is presented to assess the impact of various parameters on the thermal insulation of reinforced CLC. To achieve this, a simulation framework has been developed based on the Representative Elementary Volume (REV) analysis, Finite Element Method (FEM), homogenization algorithms, geometric optimization like Voronoi, and Discrete Element Method (DEM) for sphere packing. The methodology has been calibrated and validated using experimental results at the material, composite, and component levels. As a result, this methodology has allowed for the assessment of factors ranging from the impact of microporosity on aerogel conductivity to the effect of increasing panel thickness on the mechanical strength and insulation properties of the component. It has proven to be a powerful tool for the design and analysis of complex panels.

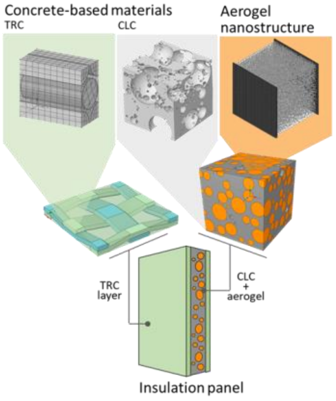

Figure 1. Scheme of the panel studied.

Besides thermomechanical behavior, future works should also include metaphysical phenomena such as fire resistance, chemical degradation, or the influence of humidity on property loss or element resistance.

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ONE-POT SYNTHESIS OF STABLE CORE-SHELL PEROVSKITE HETERONANOCRYSTALS WITH CONTROLLED PERMEABILITY TO HALIDE IONS

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Keywords: *perovskite, heteronanocrystals, controlled halide exchange*

AMatS2.- Materials for Energy.

Metal halide perovskite nanocrystals (MHP NCs) have emerged as great candidates for optoelectronic and photovoltaic applications due to their amazing optical and electronic properties.[1] More recently, they have been used in photocatalysis, such as in C-C coupling reactions.[2],[3] However, a usual drawback of MHPs is their low stability under external factors: light, humidity, and heat. Several attempts to overcome these limitations include the development of heterostructures, such as MHP NCs combined with metal oxides, halides, and ions, to produce core@shell heterodimers and nanocomposites.[4]

We envisaged that the growth of a perovskite shell on the surface of core NCs to produce core@shell HNCs could be a good alternative to overcome the poor stability of MHP NCs under environmental stress.

We will discuss here on a promising strategy to overcome the poor stability of MHP NCs, by covering a perovskite NC with a perovskite ultrathin shell to lead to a core@shell heterodimer with a minimal mismatch between the core and the shell. The great permeability of the shell enabled the formation of pure and emissive perovskite heteronanocrystals, while preserving the morphology of the pristine NCs and improving the emissive response compared to that of the related core.

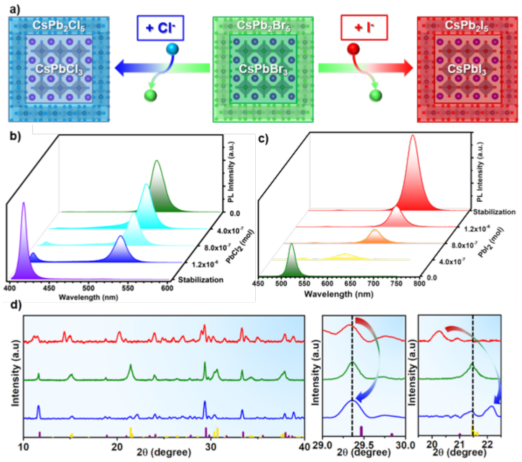

Figure 1 – a) Schematic illustration of the halide exchange process for the core@shell HNCs. Emission spectra evolution after the addition of different amounts of the lead halide and a stabilization step. d) XRD spectra of the HNCs after the halide exchange reaction. Comparison of the XRD reflection patterns to those of the bulk material of orthorhombic CsPbBr$_3$ (COD ID 1533062 – yellow line) and tetragonal CsPb$_2$Br$_5$

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DESIGN AND SYNTHESIS OF CHALCOHELICENES FOR MOLECULAR ELECTRONICS

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Keywords: *organic synthesis, chalcohelicene, molecular solenoid*

The conductance of a tunneling electron through a π-conjugated molecule may be affected by the presence of different pathways in the orbital structure of the molecule, result of the constructive or destructive interference of the molecular wave function. This quantum interference (QI) directly translates into enhancing or suppressing conductance and offers the possibility of controlling this phenomenon through tailored synthesis.[1] With this objective in mind, we did set up the synthetic methodologies to access chalcophene-fused helicenes with a well-defined positioning of the chalcogen atoms (S, Se. Te),[2] that controls the occurrence of efficient conducting pathways avoiding cross-conjugation.

In this proposal we shall describe these synthetic efforts and will relate the electronic transport through our molecules to three key variables: a) the endo-/exo- topology of the S/Se atom within the ring, b) the parity (odd/even) of the overall number of rings conforming the helicene, and c) the size of the circuit. Fig. 1 shows two of the best performing ones. Comparison of homologous dithia/selenahelicenes with identical functional groups as well as tunable HOMO/LUMO energies will allow us to isolate the key variable of bond topology from other electronic properties and face the study of QI by means of electronic transport QM simulations and actual conductance measurements on gold. Understanding and tunning the conductance in this type of molecular solenoids through QI is the main purpose of this work.

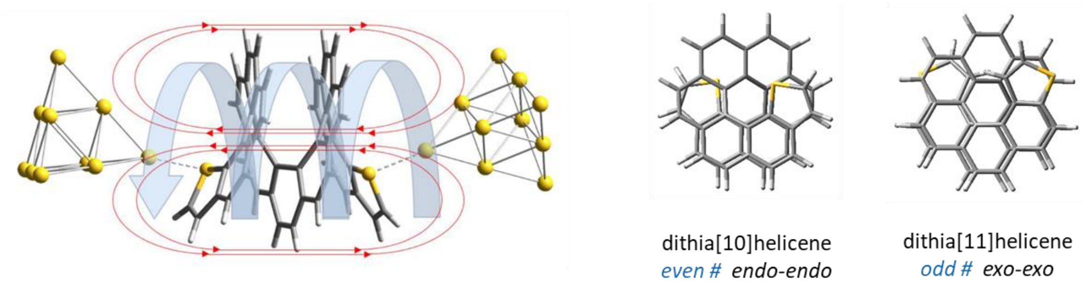

Figure 1 – A dichalcohelicene binding two Au electrodes. On the right, two of the best performing dithia/selenahelicenes found with different bond topology, parity and size of the π-system

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Uncovering the kinetics and dynamics in formamidinium lead triiodide polycrystals and their solar cell fabrication

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Keywords: Thin-film, Solar cells, *Perovskite, Stability*

AMatS2.- Materials for Energy.

In the emerging solar cells category, significant consideration has been made to investigate perovskite solar cells (PSCs) during the last decade.[1] Methylammonium lead triiodide ($MAPbI_3$) based PSCs showed competitive results initially, and this was followed by compositional engineering of the perovskites to yield higher photo-current and open-circuit voltage (V_{OC}). However, the concern of volatility and phase transformation in methylammonium (MA) and phase segregation in mixed perovskites, allowed the community to explore formamidinium lead triiodide ($FAPbI_3$) for solar cell fabrication. $FAPbI_3$ shows promising device reliability and a higher tolerance factor, further, the defects present can be suppressed by developing a powder methodology. Moreover, alloying with Cs in $FAPbI_3$ demonstrates a significant upgrade in proton diffusion rates and stability. $CsFAPbI_3$ blocks the uptake of water molecules five times higher than $FAPbI_3$. $FAPI_3$ thin films are also inclined to critical phase-transition issues owing to their thermodynamically stable non-perovskite phase (2H). We adopted a multifunctional ammonium salt-based additivization strategy to overcome this challenge, and the sulfur heteroatom present shifts the thermodynamic stability from the 2H phase to an intermediate phase closer to the cubic phase. From experimental and theoretical studies we uncover the role of Pb.S interaction in stabilizing the perovskite cubic phase and this prevents hereto unreported water and damp invasion to the formamidinium lead triiodide perovskite layer.

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Symmetrical vs Asymmetrical Metallophthalocyanines as Hole Transporting Materials in Perovskite Solar Cells

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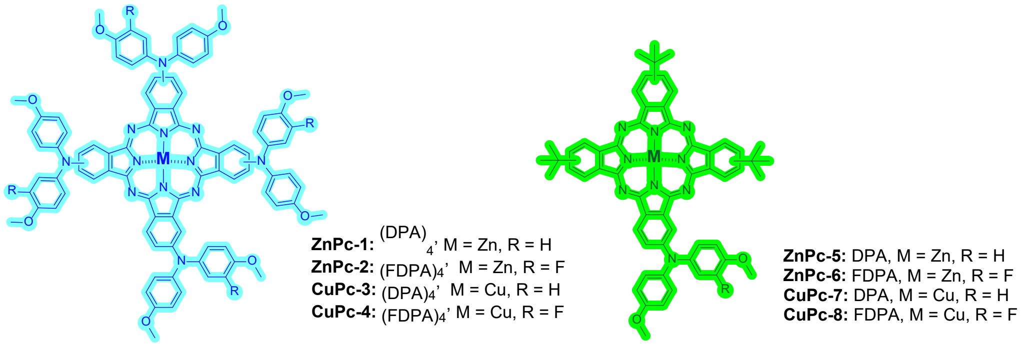
Keywords: *Phthalocyanine, Perovskite Solar Cells, Hole Transporting Materials*

AMatS2.- Materials for Energy.

Perovskite solar cells (PSCs) are promising candidates to reach the market to complement the current offer of photovoltaic cells although for such a thing they still have to overcome some challenges such as long-term stability. The hole transporting layer (HTL) is a crucial component in n-i-p PSC, since it must favor an adequate movement of charges and protect the perovskite layer from environmental conditions. In this sense, the commonly used HTL, spiro-OMeTAD, does not provide PSCs with sufficient stability and is too expensive. Cheaper molecular materials such as metallophthalocyanines are proving to be a good alternative, as they provide greater stability.[1]

In this communication, we will present novel ZnPcs and CuPcs monomers[2] (see as examples Figure 1), among others, as efficient, stable, and low cost HTMs in PSCs. The MPcs are substituted with functional groups that possesses a very good solubility in a wide range of organic solvents, adequate HOMO LUMO levels and their photovoltaics performance as high stable solution processing in a wide range of perovskite solar cell devices.



ZnPc-1: (DPA)$_4$’ M = Zn, R = H
ZnPc-2: (FDPA)$_4$’ M = Zn, R = F
CuPc-3: (DPA)$_4$’ M = Cu, R = H
CuPc-4: (FDPA)$_4$’ M = Cu, R = F

ZnPc-5: DPA, M = Zn, R = H
ZnPc-6: FDPA, M = Zn, R = F
CuPc-7: DPA, M = Cu, R = H
CuPc-8: FDPA, M = Cu, R = F

Figure 1 – Symmetrical and Asymmetrical Metallophthalocyanines

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AMatS
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RAMAN SPECTROSCOPY OF InP-InGaP HETERO-STRUCTURED NANOWIRES

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Keywords: semiconductor nanowires, Raman spectroscopy, plasmon mode, InP-InGaP.

AMatS2.- Materials for Energy.

Semiconductor nanowires (NWs) are promising candidates for the new generation of tandem solar cells [1]. Some of the advantages of nanowires are the high surface-to-volume ratios, their reduced dimension, the relaxed-lattice matching, or their behaviour as optical antennas. Also, the possibility of tailoring their optical and electronic properties by changing their geometry, crystalline structure, and/or doping only broadens their spectrum of applications. Finally, their low dimension makes the nanoscale analysis crucial to accurately probe their structure, composition, or doping profiles.

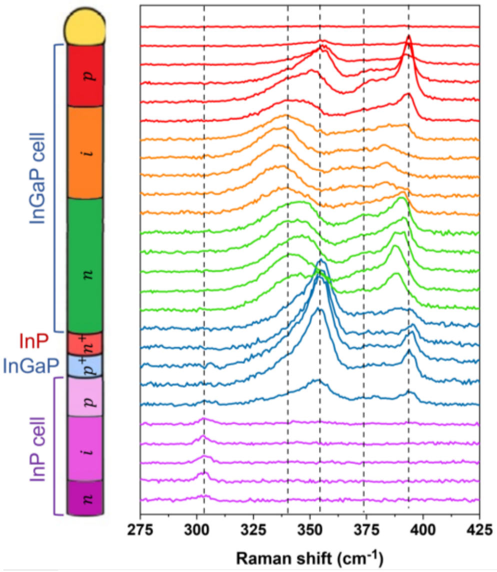

Figure 1 – Raman spectra recorded along the NW showing the different sectors of the NW with different colors.

Herein, we report the Raman analysis of a single InP-InGaP heterostructured NW connected by a tunnel diode (Fig.1). This technique allows for the structural and compositional characterization of the nanowire, enabling the analysis of the different sectors constituting the nanowire.

The bottom cell of InP shows a Zinc-Blende structure, identified with the transverse optic (TO) phonon peak at 304 cm^{-1} (purple spectra). On the contrary, from the analysis of the top cell, we have identified how doping affects the incorporation of indium during the growth process, resulting in a non-uniform composition. The p-type doping (Zn) reduces indium incorporation, while the n-type doping (S) does not introduce significant changes.

The most appealing results have been obtained when analysing the tunnel junction (blue spectra), where a significant increase of the Raman signals is observed. This enhancement allows us to identify a Raman mode that can be associated with a LO phonon plasmon coupled mode which permits us to characterize the tunnel junction.

This analysis has provided us with a comprehensive picture of the composition of the nanowires, the successful growth of the tunnel diode, and the effect of doping on the composition of the alloy.

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AB-INITIO THERMAL TRANSPORT CALCULATIONS FOR CRYSTALS AND NANOSTRUCTURES

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Keywords: *thermal conductivity, phonons, Boltzmann transport equation, density functional theory*

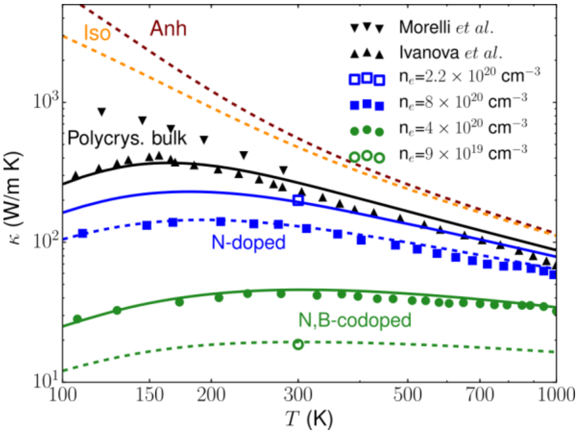
AMatS2.- Materials for Energy

Understanding and controlling thermal transport is a requirement for optimizing the performance of waste-heat scavenging with thermoelectric generators, as well as for developing efficient and long-lasting electronic components. In this context, predictive theoretical methods have an important role to play by enabling the *in-silico* design of materials and structures for specific applications.

When the systems concerned are derived from semiconducting crystalline solids, solutions of the Boltzmann transport equation (BTE) based on input data from density functional theory (DFT) offer a very interesting balance of cost and predictive power. In the last decade, the range of applicability of that formalism has been greatly extended to encompass not only crystalline solids in the steady state, but systems with defects, heterogeneous structures and time-dependent phenomena. In this presentation I will briefly discuss a selection of applications to highlight the excellent agreement with experiment that can be obtained without any fitting parameters. I will emphasize how thermal conductivity measurements can be used to help determine the kind of defects contained in a sample. These calculation methods are implemented in ShengBTE and almaBTE [1], two open-source software packages that I co-developed to make these workflows available to the community.

I will conclude by summarizing some of the outstanding challenges in this area, and how machine-learning techniques can help overcome them.

Figure 1 – Comparison between ab-initio and experimental results for doped 3C-SiC, adapted from [2]



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POSTERS – LA2

ACOUSTIC MONITORING OF WIND GENERATOR BLADE MACHINING USING ULTRASHORT PULSE LASERS

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Keywords: *Wind generation, Ultrashort pulse lasers, Antiicing, Acoustic Analysis*

AMatS2.- Materials for Energy.

Wind generators performance can be affected by ice generation on the surface of the blades. Different active and passive solutions are currently being assessed in order to minimise these effects. Passive solutions are based on the modification of surface properties, for instance, hydrophobicity and icephobicity. In this context, laser surface modification is an environmentally attractive option.

The external surface of a wind generator blade consists of ceramic particles embedded in a polymeric matrix. This type of microstructure presents a challenge for the development of laser machining protocols that can modify surface properties in a controlled manner, as the ablated regions tend to be inhomogeneous. The use of ultra-short pulse lasers enables the development of micromachining processes which reduce or avoid the appearance of severe heat affected zones, thus improving the quality of the remaining surface microstructure [1]. By adjusting the laser processing parameters, it is possible to obtain superhydrophic surfaces which improve with time.

This work demonstrates that acoustic recording is a powerful tool to monitor the ablation processes associated with laser machining. A correlation between the acoustic intensity and the depth of the ablated region has been established with a precision of about 2 μm. This is difficult to achieve using other non-destructive techniques, such as confocal microscopy. More importantly, the acoustic recording provides this information in the overall sample and in-situ/operando, i.e. while performing the machining process. In addition, acoustic recording can be used to identify different ablation mechanisms generated during laser processing. Several experiments using lasers with three different wavelengths (1030, 515 and 343 nm) and with different levels of power and frequencies have been performed while the sound has been simultaneously recorded. The transition between different machining mechanisms has been identified by analyzing the correspondingly observed acoustic dependencies.

These results suggest that acoustic recording may pave the way towards implementation of an on-line monitoring technique. The latter provides in-situ, real time information on the evolution of laser machining processes as well as on the mechanisms that may govern them.

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A MULTI-LEVEL THEORETICAL APPROACH FOR THE CHARGE TRANSPORT CHARACTERIZATION IN PROMISING HOLE TRANSPORT MATERIALS

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Keywords: *HTMs, charge transport, spiro-OMeTAD, IDIDF*

AMatS2.- Materials for Energy.

In recent year, Material Science has been a great ally in the fight against the climate change; more specifically, in the field of energy conversion. Hole Transport Materials (HTMs) are an essential component of the photovoltaic devices. HTMs work as an active layer to transport the generated hole carrier from the photovoltaic material (dye or perovskite) to the electrodes, as well as a physical barrier between these two components. In this work, we propose a multi-level theoretical approach to calculate and predict the carrier mobility in HTMs. A series of electronic structure calculations –based on hybrid DFT-, molecular dynamics and Kinect Monte Carlo simulations, and real space analysis were applied to two promising and significantly different HTMs: spiro-OMeTAD[1] and IDIDF[2] (Figure1). Experimental results, in thin-film devices, show that the hole mobilities in the IDIDF are greater than those observed in the spiro-OMeTAD, 1.7×10^{-3} and 4×10^{-5} cm^2 V^{-1} s^{-1}, respectively [3]. We found that, despite the difference between spherical and planar shape, there is a strong direction-dependent charge transport in the two HTMs. The NCI analysis shows that the intermolecular interactions are a necessary but not sufficient condition for large electronic couplings. By applying a Kinetic Monte Carlo simulation, based on a statistical analysis of the site energy and electronic couplings, we can reproduce the resulting mobilities in the spiro-OMeTAD and IDIDF materials. As expected, both HTMs present a reduction on the hole transport properties upon including the dynamic disorder promoted by finite temperature effects. Finally, in good agreement with the experimental data registered in thin-film devices, the impact of the material amorphousness in the hole mobility was calculated by modelling a fully random distribution of the molecules; mobilities of 1.1×10^{-3} and 4.9×10^{-5} cm^2 V^{-1} s^{-1} were obtained for IDIDF and spiro-OMeTAD, respectively[4]. These results confirm the excellent charge transport properties of the indoloindole-based HTMs for future applications in organic electronics and photovoltaics.

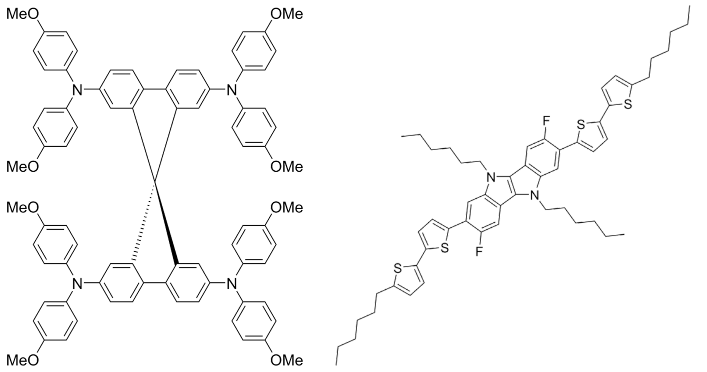

Figure 1 – Left: Spiro-OMeTAD, right: IDIDF

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Caesium Bismuth perovskites: From bulk to Nanocrystals materials for optoelectronics applications

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Keywords: *Inorganic Perovskite materials, Nanocrystals, Thin-Films, solar cells*

AMatS2.- Materials for Energy.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: YES/NO

ABX_3 perovskites have been intensively studied due to their exceptional optoelectronic properties. However, concerns over the materials instability and toxicity of the commonly used lead halide perovskites have led to the development and characterization of new alternative perovskite materials.[1-3] Among the new materials developed Bismuth-based perovskites are considered to be one of the promising candidates retaining excellent optoelectronic properties while being environmentally friendly and showing stability to heat, moisture and light.[2] Bismuth-based all inorganic ternary perovskite $Cs_3Bi_2Br_9$ has been extensively studied, demonstrating good optoelectronic properties photostability & moisture stability,[1,2] for solar cells, light-emitting diodes and photodetectors.[2] However, the bandgap of the $A_3B_2X_3$ structures is relatively wide due to the higher electronegativity of the halogen and thus developing methods to control the bandgap is of particular interest.[1,2] The calculated indirect electronic gap of $Cs_3Bi_2Br_9$ is 2.55 eV, and a direct optical gap of 2.66 eV, which is higher than the desirable 1.3 eV. Common methods to control the bandgap of the material are halide alloying and doping on the B-metal site with perovskites.[1,2] Here, we focused our efforts on doping of $Cs_3Bi_2Br_9$ with Cu(I), Cu(II), and Mn(II) cations to produce strain in the crystal structure and deduce small shift in the diffraction pattern without causing a change of crystal phase. With an aim to tune the bandgap of the material to shift the absorption and gaze the changes in the electronic bandgap from indirect to direct. Further these developed materials have been explored for memristors and photovoltaics applications.

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Electrochemistry for biomass valorization and energy storage

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Renewable energy sources are indispensable for facilitating the transition to a sustainable and environmentally friendly energy system, thus diminishing our reliance on fossil fuels. However, a notable drawback of renewables lies in their intermittent nature, heavily contingent on climate conditions. This intermittency results in a significant disconnect between energy generation and demand.

Electrochemistry, powered by renewable sources, has emerged as an intelligent solution that can pave the way for this crucial energy transition. Electrochemical processes play a pivotal role in harnessing energy from renewable sources. The primary chemical reactions under scrutiny in electrochemistry encompass water splitting and CO_2 reduction. In both of these processes, the pivotal oxygen evolution reaction (OER) unfolds at the anode. This OER step furnishes the essential electrons and protons necessary at the cathode for either generating hydrogen (H_2) or converting carbon dioxide (CO_2) into valuable compounds such as methane (CH_4) or methanol (CH_3OH).

It is noteworthy, however, that despite the pivotal role of O_2 production in the OER, the market value of oxygen remains disproportionately low. This economic disparity challenges the feasibility of processes reliant on OER and, consequently, diminishes interest in this technology.[1] Additionally, the OER tends to exhibit substantial overpotentials when utilizing catalysts composed of abundant Earth materials, thereby curbing overall energy conversion efficiency.[2]

Given these compelling reasons, there is a burgeoning interest in identifying alternative anode reactions. Such reactions should not only reduce the requisite overpotentials but also yield compounds of greater intrinsic value, thereby enhancing their appeal to the chemical industry.[1-3] In this context, biomass valorization has emerged as a particularly attractive alternative to conventional water oxidation.[4]

Herein we present our latest findings in the electrochemical transformation of biomass, as well as explore the application of electrochemistry for energy storage purposes.

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Fabrication and Characterization of Calcium Cobaltite and Calcium Manganite-Based Thermoelectric Module for Sustainable Energy Generation

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Keywords: *Thermoelectric module, Calcium cobaltite, Calcium manganite, Energy conversion.*

AMatS2.- Materials for Energy.

As the world's population is increasing rapidly, the necessity for energy is growing up by alarming rate. Considering the limited traditional energy sources and their effects on global warming due to CO_2 emissions, finding alternative green energy sources is crucial. On the other hand, since more than 65% of the energy used in different sectors is wasted in the form of heat, extensive research in the field of thermoelectric materials as a promising technology for efficient energy recover is being done as they can directly transform heat to electricity [1].

In this study, we present the fabrication and characterization of a thermoelectric module utilizing p-type Sr-doped calcium cobaltite ($Ca_3Co_4O_9$) material, and n-type Ce-doped calcium manganite ($CaMnO_3$) one [2]. These materials have shown promising thermoelectric properties, making them suitable candidates for applications in waste heat recovery and sustainable energy generation.

Both type of precursors were prepared through the attrition milling procedure, which allows a drastic decrease in thermal processing time. The p-type material was prepared using hot pressing to achieve dense pellets, using the procedure previously described [3], while the n-type materials were sintered [2]. All the thermoelectric properties (Seebeck coefficient, electrical conductivity, and thermal conductivity) were measured for both compounds. These prepared legs were then assembled into a thermoelectric module pattern using the electrical series-thermal parallel configuration, involving silver paste as a precursor for electrical interconnections. Finally, the module was characterized using a home-made system, cooling the cold side at about 18 ºC using a flowing water circuit, and heating the hot side to temperatures between 200 and 900°C.

The results demonstrate the potential of these thermoelectric modules to convert heat into electricity efficiently. This research contributes to the ongoing efforts in developing advanced materials for energy conversion and highlights the promise of calcium cobaltite and calcium manganite-based thermoelectric modules in addressing the global energy sustainability challenge.

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FUNCTIONAL 2D Na-Mn-O SYSTEMS FOR HIGH PERFORMANCE AND LOW COST SODIUM ENERGY STORAGES

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Keywords: *sodium manganese oxide, aqueous capacitors, cycling voltamperometry*

AMatS2.- Materials for Energy.

In recent years, the use of portable energy sources has been growing exponentially. According to forecasts, at current levels of consumption, lithium reserves will be exhausted in a few years. That is why many scientific developments concern Na ion batteries and capacitors. In both cases, Li or Na, the main reaction is ion intercalation, which provides high capacity. However, the large difference in the ionic radii of lithium and sodium does not make it possible to use materials with a channel structure in sodium-ion devices. The best candidates are layered structures based on transition metal oxides. In addition, the battery-type electrode must have stable structure, high electrochemical potential and an optimal surface area. The paper describes the synthesis of 2D polymorphic phase modifications of sodium containing manganese oxide, its layered structural and morphological characteristics, and their use as an electrode material for aqueous energy storages.

Samples of sodium manganese oxide with different amounts of sodium have been prepared using a sol–gel method with a final annealing temperature of 750 degrees. The XRD patterns of the as-synthesized Na_xMnO_2 (x=0.8;1.0;1.2) are shown in Figure 1a. Final annealing at a temperature of 750C leads to the formation of low-temperature (ICSD 21028) and high-temperature (ICSD 16271) polymorphous phases combination depending on the sodium content. The cyclic voltammetry tests were performed using a three-electrode cell using Pt wire and Ag/AgCl electrode as counter and reference electrodes, in an aqueous solution of 1 M Na_2SO_4 Na_2CO_3 and $NaNO_3$ (0,5 - 50 mV/s).

Based on CVA, it is proved that the total capacitance is provided by intercalation and pseudo-capacitance. The maximum capacitance values were calculated for the sample with the highest stoichiometry and optimal morphology. These electrodes were also cycled and after 100 cycles (Figure 1b) the lowest capacity loss was recorded for sodium sulfate. This confirms the existence of the intercalation process and the stability of intercalation/pseudocapacitance during long-term cycling.

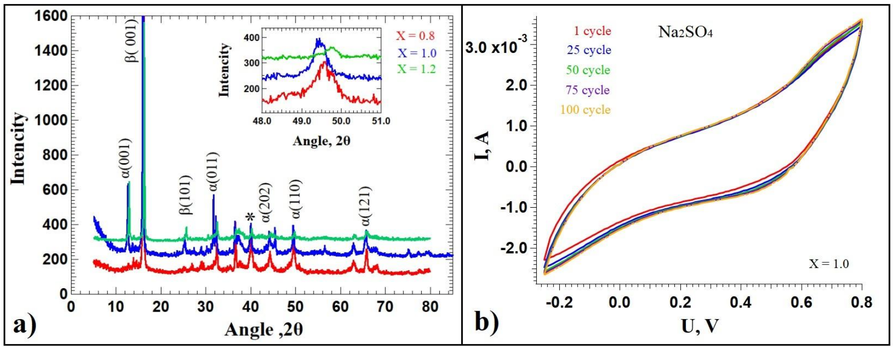

Figure 1. (a) XRD of samples; (b) CVA after 100 cycles in Na_2SO_4.

HYDROGEN EMBRITTLEMENT MECHANISMS OF A 2205 DUPLEX STAINLESS STEEL

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Keywords: *Hydrogen embrittlement, 2205 Duplex steel, in-situ hydrogen tests*

AMatS2.- Materials for Energy.

2205 duplex stainless steel has been widely used in petrochemical industry and marine environments because of their outstanding strength, weldability, and corrosion resistance in chlorine environments. However, 2205 DSS is sensitive to hydrogen embrittlement what has limited its use to work in hydrogen environments at high pressure [1,2].

In this work, hydrogen embrittlement (HE) susceptibility of a 2205 duplex stainless steel has been evaluated by means of in-situ tensile tests. Tests have been performed in a High-Pressure hydrogen autoclave at the Hydrogen Research Laboratory (H2Lab) of the University of Burgos (Spain). Tests were carried out on smooth and notched specimens at different pressures, in order to study the notch effect in the hydrogen embrittlement susceptibility. In all samples the loading direction is parallel to the ferrite/austenite banded microstructure, resulting in cracks perpendicular to the cross section.

For tests conducted on smooth specimens, without hydrogen, a ductile fracture micromechanism characterized by growth and coalescence of microvoids was observed. For in-situ H2 tests, at pressures of 70 and 140 bar, hydrogen-assisted cracks were initiated over the entire surface. Ferrite cleavage-like fracture and austenite quasi-cleavage fracture with small breaches are observed [2]. YS and UTS are 'slightly' affected by hydrogen. However, HE is mainly marked in terms of the elongation (ε) and reduction of area (RA). Despite of this, the increase in H2 pressure from 70 to 140 bar seems to be negligible.

For the notched specimens, with a notch factor K_t=5.6, the effect of pressure seems to play now an important role on the embrittlement process. For the uncharged specimens, fracture surface also showed clear dimples, indicating ductile fracture behaviour. However, for H2 in-situ tests at 70 bars, two different operative failure micromechanims were observed. In the outer zone, a brittle region (200 μm depth) was observed, with secondary cracks growing internally. Nevertheless, dimples were also observed in the centre of the specimen. For H2 in-situ tensile tests at 140 bars, hydrogen-assisted cracks nucleate directly from the notch tip surface. At higher magnification, flat cleavage facets in the ferrite and a rougher surface in the austenite are clearly observed. At 140 bar, the UTS and RA were notably affected by hydrogen.

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Interplay between ion migration and Contacts in Halide Perovskite Electronic Devices

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Abstract

Halide perovskite materials find applications in solar cells, X-Ray detectors or memory storage devices. This type of perovskites are mixed electronic and ionic conductors that typically display a strong hysteresis during the electrical characterization.[1, 2] The ionic conductivity is responsible for a memory effect that leads to undesirable hysteresis in the solar cell configuration. Alternatively, in the resistive memory configuration this hysteresis is a requirement and needs to be well understood to offer a good control of the conductive states. Here, we show that the working mechanism and performance of the memory devices can be tuned and improved by a careful selection of each structural layer. Several configurations are evaluated in which structural layers are modified systematically: formulation of the perovskite[3], the nature of the buffer layer[4] and the nature of the metal contact[5]. Overall, we provide solid understanding on the operational mechanism of halide perovskite memristors that unveils the connection between electronic and ionic conduction.

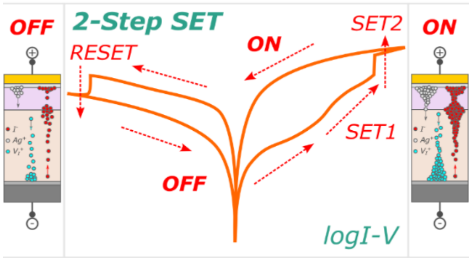

Figure 1: Example of a two-step activation mechanism promoted by the selection of the buffer layer.[3]

Acknowledgements

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Investigation of Structural and Electronic Properties of $NaMgH_3$ for Hydrogen Storage

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Keywords: *Hydrogen energy, Hydrogen storage, Ab initio calculations, Structural properties, Electronic properties*

Sodium magnesium hydride $NaMgH_3$ is one of the promising candidates for hydrogen storage applications. The structural and electronic properties of $NaMgH_3$ have been thoroughly examined using density functional theory. The generalized gradient approximation (GGA) has been employed to achieve satisfactory agreement concerning the bulk crystal structure.

Parameters such as lattice constant, bulk modulus, and electronic band structures are calculated and compared with available experimental and other theoretical data. Analysis of the electronic density of states (DOS) reveals a predominance of hydrogen atoms in the valence band, while Na and Mg empty states take precedence in the conduction band.

Furthermore, the DOS sheds light on the insulating nature of $NaMgH_3$, characterized by a wide bandgap and a direct band gap of 3.4 eV.

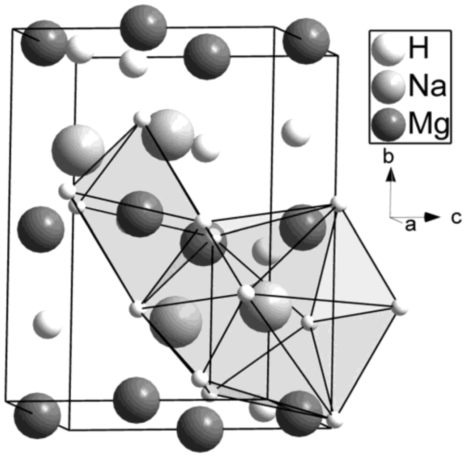

Figure 1 – The crystal structure of the orthorhombic perovskite NaMgH3 in the $GdFeO_3$ type structure.

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AMatS
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NEW MATERIALS FOR FATIGUE ASSESSMENT OF COMPOSITE TIDAL TURBINE BLADES

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Keywords: *InterLaminar Crack propagation (ILC), Adhesive Interface Crack propagation (AIC), durability assessment, composite damage*

The growing global demand for renewable energy sources has led to an increased focus on harnessing ocean energies using tidal current turbines. In recent years, there has been a significant rise in interest in this technology because it is a highly predictable energy source and water is hundreds of times denser than air, which makes tidal energy more powerful than wind. It also produces no greenhouse gases or other waste. Despite the advantages associated with tidal power systems, the high levelized cost of energy (LCoE) from tidal stream turbines has resulted in lower-than-expected installations of megawatts (MW) in Europe in recent years.

The major reason for this is the high cost of installation and maintenance in the sea water environment which is critically dependent on the failure rates of the turbine blades. A possible way to minimizing the LCoE and improving the availability of tidal turbines for energy generation is the extension of blade fatigue life by means of **appropriate material selection and structural integrity and durability assessment.**.

Within the EU-funded NEMMO [1] project an advanced procedure for the estimation of tidal turbine blades' life under damage tolerance considerations has been developed. This procedure consists of two main stages: the first one includes **experimental protocols** to understand the static and dynamic fracture mechanical behaviour of a new additive-reinforced novel multi-layered cross woven composite [2]; the second one considers a **finite element-based methodology** that allows to locate the critical sections for the delamination and debonding failure modes and the estimation of the life in terms of number of cycles of the blade from crack initiation to failure for a given load spectrum [3].

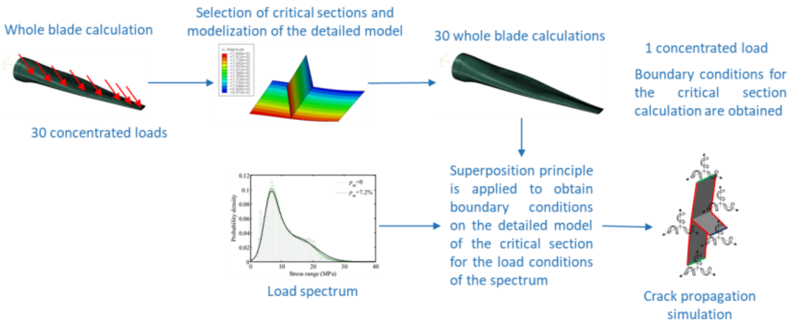

Figure 1 – Outline of the proposed methodology

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Optical Properties and Fano Resonance Behavior in Silicon Nanowires with p-n Junctions: Mapping the Transition

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Keywords: *Silicon Nanowires, Raman spectroscopy, p-n junctions, Fano resonance*

AMatS2.- Materials for Energy.

In recent years, nanowires (NWs) have received a great deal of research attention due to their unique physical and optical properties. In particular, Si NWs with homojunctions have shown higher forward current density than typical bulk silicon p-n junctions, with low absorption losses, making them highly attractive for photovoltaic applications. In these devices, understanding the role of dopants and their interaction with the structures is crucial to develop more efficient solar cells. Electrical measurements, e.g. Hall effect, are difficult to perform in this tiny structures. Contactless microRaman spectroscopy can be used for the characterization of Si NWs. It provides structural characterization through its vibrational modes, and permits the estimation of the free carrier concentration through the Fano resonances [1]:.

$$I(\omega) = A\frac{(q+\varepsilon)^2}{(1+\varepsilon^2)}\,;\ \varepsilon \equiv \frac{\omega-\omega_0}{\Gamma} \qquad \text{(eq. 1)}$$

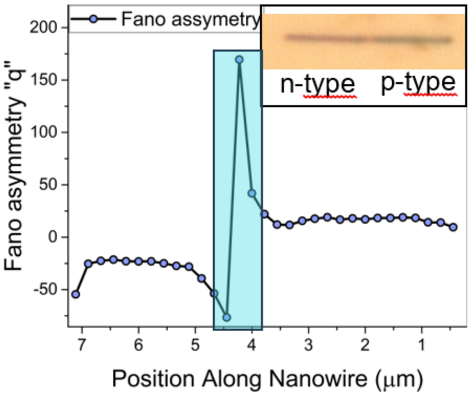

Figure 1 – Fano behavior along a Si p-n NW

We present here the microRaman characterization of silicon nanowires (Si NWs) with axial p-n homojunction.

Fig.1 shows the Fano asymmetry parameter, q in eq. 1, calculated from the Raman spectra recorded along a Si NW 7 μm long. We can appreciate the transition from the n-type to the p-type segment zone. q is negative for n-type and positive for p-type. The smaller (in absolute value) the q parameter, the higher the concentration of free carriers. The high values of q values of q (up to 100) correspond to a symmetric Lorentz lineshape of the Raman peak, revealing charge depletion. The Raman scan along the NW reveals the n-type segment (negative q), the charge depleted junction (Lorentz lineshape), and the p-type segment (positive q). It should be noted that the Lorentzian lineshape was observed in one single measurement point. Taking account of the laser diameter (≈ 0.8 μm) the observation of the Lorentzian spectrum in the junction points to a laser beam confinement in the tiny carrier depleted junction. Moreover, one can see how the free carrier concentration decreases (higher absolute value of q) around the junction for both the n-type and the p-type segments. One can estimate the free carrier concentration from the q value. The hole concentration in the p-side is estimated at ≈1.2 x10^{19} cm^{-3}. Micro Raman spectroscopy can be used as a contact less for the free carrier estimation in doped semiconductor NWs, it permits the characterization of the junctions, which is allowed by the electromagnetic resonances in the dielectric discontinuities of NWs

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POLYMER COATINGS BASED ON NANOENCAPSULATED PHASE CHANGE MATERIALS FOR LATENT HEAT STORAGE

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Keywords: *phase change material, coating, miniemulsion, polymerization, energy storage*

AMatS3.- Smart materials with advanced functionalities. (TICs, Biomaterials, Mobility, Habitat and environment)

In recent years, there has been a significant increase in the development of systems for energy storage, driven by the need to address the persistent timing misalignment between energy production and demand that renewable energy sources often experience. Within this context, phase change materials (PCMs) have emerged as highly promising systems. These materials have the capacity to store thermal energy in the form of latent heat during a phase change and release it when returning to the initial phase [1, 2]. PCMs play a crucial role in addressing the challenge of storing and utilizing thermal energy effectively, especially in applications where maintaining a stable temperature is essential. PCMs have the potential to contribute to energy conservation, sustainability, and enhanced comfort in a wide range of industries and technologies, including construction, packaging, and textiles. In many of these applications, formulating the materials as coatings is useful.

This investigation focuses on encapsulating solid–liquid organic PCMs, namely alkanes such as hexadecane and octadecane, by using miniemulsion polymerization (radical polymerization or oxidative polymerization, depending on the aimed polymer). These linear alkanes are attractive PCM options for numerous applications due to their excellent thermal conductivity and high efficiency in storing substantial amounts of heat at temperatures close to room temperature. Encapsulating alkanes within polymer capsules offers several benefits, including easier processing, prevention of leaks, protection of the surrounding environment from adverse effects, and ensuring the recyclability of the process. In addition to commonly used structural polymers, such as polystyrene, we have also explored capsules made of conductive polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT). With the use of PEDOT, the features of thermal energy storage provided by the encapsulated PCM can be combined with the thermoelectric ability of the conductive polymer.

This work also addresses the formation of various coatings containing the encapsulated PCMs. First, polymer films were produced by drop-casting with the redispersion of the PCM capsules in a polymer solution. Second, PCM capsules were applied to textile fabrics using the layer-by-layer (LbL) technique. The effectiveness of these prepared nanocomposites for energy storage applications was assessed through differential scanning calorimetry (DSC) and proof-of-concept devices.

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PSEUDOCAPACITY AND INTERCALATION IN AQUEOUS SODIUM ION ENERGY STORAGES: INVESTIGATION DURING OPERATING OF 2D $NaMnO_2$

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Keywords: *2d materials, aqueous energy storages, intercalation, pseudocapacitance*

AMatS2.- Materials for Energy.

The main reaction of any electrochemical system is the ion intercalation (lithium, sodium, zinc) during discharge and its extraction during charging. However, this is an ideal case that does not take into account the effect of absorption of these ions on the surface. This is especially important for the devices operation in aqueous electrolytes and also at high operating currents or cycling speeds. Therefore, it is important to establish the part of intercalation (solid state ion diffusion) and the share of capacity provided by the formation of a layer on the surface (pseudocapacitance). For this purpose, a set of studies of electrochemical systems based on layered sodium manganese oxide in aqueous electrolytes was carried out. The cyclic voltammetry (CVA) tests were performed in an aqueous solution of 1 M Na_2SO_4, Na_2CO_3 and $NaNO_3$ (100 cycles, scan rate 50 mV/s). XRD, XPS and SEM and EIS were measured before and after cycling.

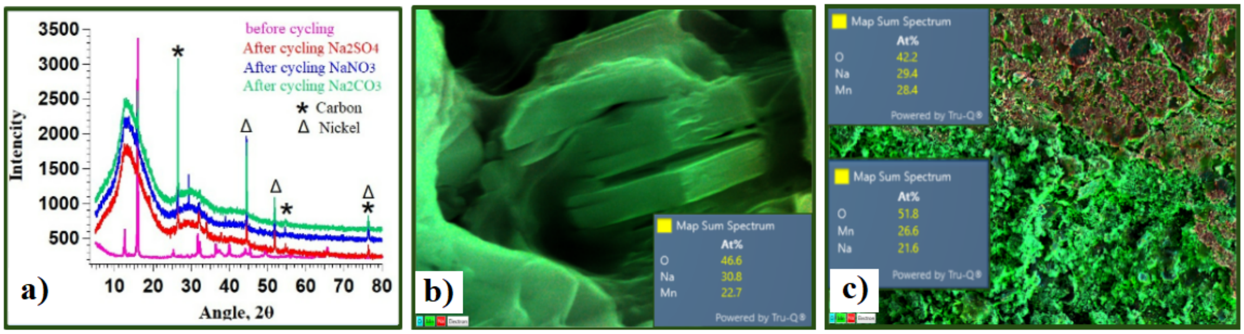

Figure 1. (a) XRD of electrode after cycling; (b) SEM image of $NaMnO_2$ particle after cycling ; (c) SEM image of electrode surface after cycling

Total capacitance for 2D Na-Mn-O systems in aqueous electrolytes is provided by intercalation and pseudocapacitance. The ratio depends on the structure, morphology of electrode solution and the type of electrolyte. For all electrolytes, we observe the formation of an amorphous film that stabilizes by cycling. After cycling at a high scan rate, we do not see degradation of the structure and additional XRD peaks of the active layered $NaMnO_2$ (Figure 1a) Based on SEM, a large part of the sodium ions we observe on the upper part of the electrode, which provides pseudocapacitance (Figure 1c). We also see intercalation into the upper layer of particles of active materials under the passivation film(Figure 1b).

REDOX ACTIVE NANOCRYSTALS AND ELECTROLYTE TO FOR A HIGH ENERGY AQUEOUS SUPERCAPACITOR

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Keywords: *Nanocrystals, Nanomaterials, Supercapacitors, Energy storage*

AMatS2.- Materials for Energy.

The development of novel, reliable, environmentally friendly, and inexpensive energy storage systems has become a priority for the scientific community. Among them, electrochemical supercapacitors show short charge/discharge times, high energy density, and long lifetime when compared to batteries.[1]

Standard supercapacitors use organic electrolytes such as acetonitrile or propylene carbonate that provide high operational voltage windows but show other limitations such as toxicity and flammability. The use of aqueous electrolytes reduces the voltage, requiring an improvement of capacitance to maintain high energy outputs.

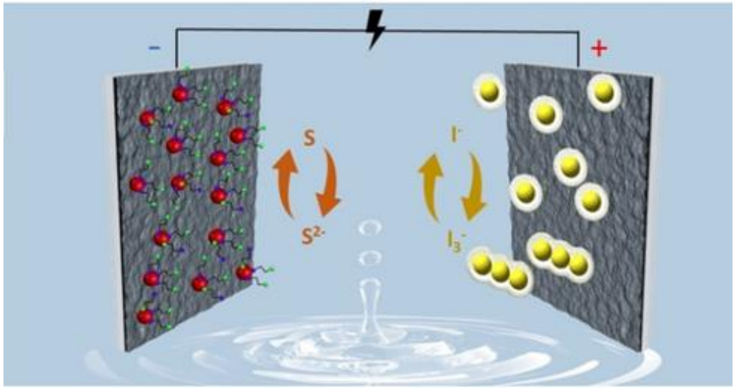

Figure 1 – Schematic representation of the double redox aqueous supercapacitor

With the aim of developing high capacitance materials for their use as electrodes in aqueous supercapacitors, a commercial porous carbon has been functionalized with chalcogenide semiconductor nanocrystals showing redox activity. The combination of this hybrid material in the electrode with a redox active iodide-based electrolyte has led to a double redox aqueous supercapacitor with a specific energy output of 20 $Wh \cdot kg^{-1}$, analogous to organic capacitors.[2]

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Relaxed requirements for viscous electron flow

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Viscous flow of interacting electrons in two dimensional materials [1,2] features a bunch of exotic effects. A model akin the Navier-Stokes equation for classical fluids accounts for them in the so-called hydrodynamic regime. This regime occurs when electron-electron collisions are frequent enough. We performed a detailed analysis of the hydrodynamic requirements and found three new routes to achieve viscous electron flow [1]: favoring frequent inelastic collisions, the application of a magnetic field or a high-frequency electric field. More reflective edges of the material further span the range of validity of the above conditions. Our results show that the conventional requirement of frequent electron-electron collisions is too restrictive, and, therefore, materials and phenomena to be described using hydrodynamics are widened. We discuss recent experiments regarding Poiseuille-like flows [3], superballistic conduction and negative resistances as signatures for viscous flow onset [4]. We conclude that these usual signatures of viscous electron flow are achieved by following alternative meta-hydrodynamic routes.

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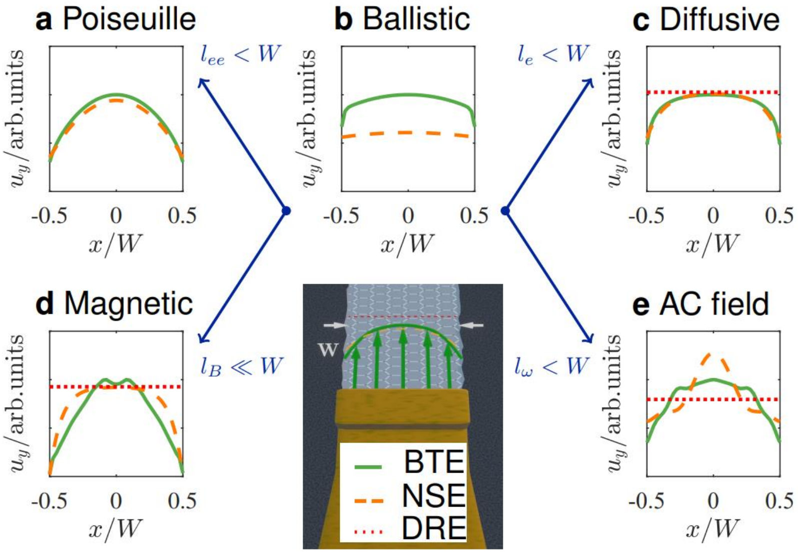

Figure 1: transverse velocity profile in a channel by different transport regimes. Pannels (c)-(e) show the accuracy of the hydrodynamic model to reproduce the curved velocity profile in the new meta-hydrodynamic routes.

THERMOELECTRIC STUDY OF THE POLYMERIC SYSTEM FORMED BY POLYVINYLIDENE FLUORIDE (PVDF) AND PHOSPHORIC ACID (H_3PO_4) FOR A FUTURE IMPLEMENTATION IN A HIGH TEMPERATURE FUEL CELL

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Keywords: *PVDF, H_3PO_4, ionic conductivity, impedance spectroscopy, fuel cell.*

AMatS2.- Materials for Energy.

In the case of a poster contribution indicate if you are interested in participating in the Poster Flash/Elevator Pitch session: NO

Proton exchange membranes composed of polyvinylidene fluoride (PVDF) and phosphoric acid (H_3PO_4) were prepared in various concentrations (Acid/Polymer): 0.08, 0.15, and 0.20. The results in differential scanning calorimetry (DSC) show a thermal anomaly around 160 C attributed to the softening temperature or T_m of the pure polymeric membrane. No relevant changes are observed in the different membranes with acid for the T_m. No thermal anomalies associated with the glass transition temperature (T_g) were observed, possibly due to the temperature measurement range performed on the samples, which ranges from 30 C to 300 C. On the other hand, complex impedance measurements were performed. in frequency sweeps from 42 Hz to 5 MHz, in a temperature range between 25 C and 70 C on the various samples, yielding results between 10 2 $^{\Omega}$ and 10^{4} Ω and whose value is possibly attributed to the water content in the sample. polymeric membrane since in the presence of phosphoric acid, this system becomes hygroscopic. Samples without moisture present impedance values of the order of 10^{6} Ω. After performing the adjustment and data analysis, it was possible to determine a mean value in the activation energy attributed to the H^{+} radicals , around 0.8 eV. The results in the imaginary part of the electrical module vs. frequency (M " vs. v) show a single peak-shaped behavior indicating a single type of ion dynamics in the bulk of the material. Morphological characterization measurements were also performed using the scanning electron microscopy technique (SEM) which allowed to identify larger pores with the increase in the acid concentration on the membranes, favoring ionic mobility. Finally, all these studies are carried out with the aim of an application in fuel cells given the limitation in the density of current that commercial cells based on Nafion have working at more than 35 C.

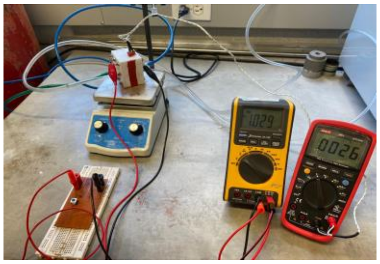

Figure 1. Fuel cell

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UPCONVERSION LUMINESCENCE IN A DYE-LANTHANIDE MOLECULAR SYSTEM

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Keywords: *Xanthenic dye, lanthanide, upconversion, cooperative sensitization.*

AMatS2.- Materials for Energy.

Xanthenic dyes, such as EOS Y(EOS) have attracted the attention of researchers in materials science because they have diverse applications, such as components of microchips, in sensor devices, and fiber optics.[1]

NIR-Vis upconversion emission has been reported for a β-diketonate Yb^{3+} complex/rubrene pair, which emits in the yellow under NIR excitation. This process occurs via a NIR−Vis TTA mechanism and requires an emitter, such as rubrene, whose triplet excited state has a lower energy than that of the Yb^{3+} excited state ($^*Yb^{3+}$).[2]

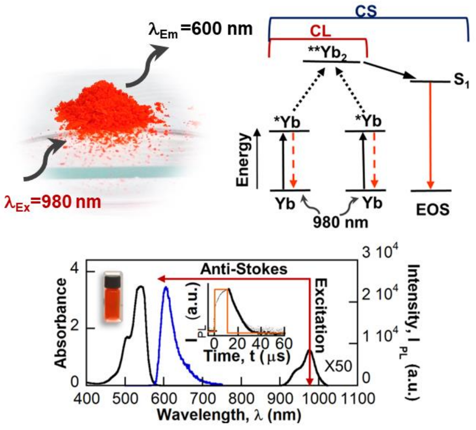

Figure 1 – Scheme of Cooperative Sensitization Upconversion in dye-lanthanide system

Interestingly lanthanide ions, such as Yb^{3+}, can absorb NIR photons, they are photostable, and their excited states are long-lived. The process occurs via cooperative luminescence (CL) that takes place upon simultaneous NIR-excitation of two close-lying Yb^{3+} ions, thus leading to an upconverted quasi-virtual $^{**}Yb_2$ excited state, which can emit one photon with almost twice the energy.[3]

Here we combine the best of both worlds (xanthenic dyes and lanthanides) and demonstrate the efficient cooperative sensitized upconversion of the dye after NIR excitation. Remarkably, the EOS dianion emission exhibits a nearly linear dependence on the EOS-Yb concentration and a quadratic dependence on the laser power density. The emission is non-sensitive to oxygen and its lifetime lasts about 1.76 μs and 12 μs in DMSO and DMSO-d_6, respectively. [4]

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