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# NanoSpain Conf 2023

April 25 - 28, 2023 • Tarragona (Spain)

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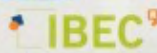
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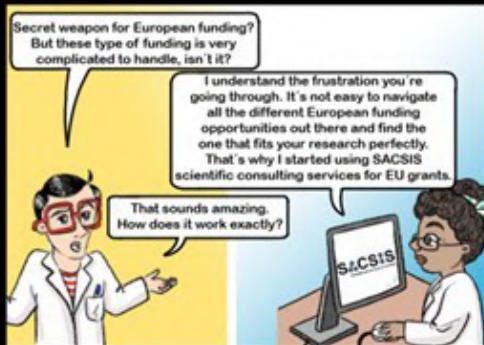
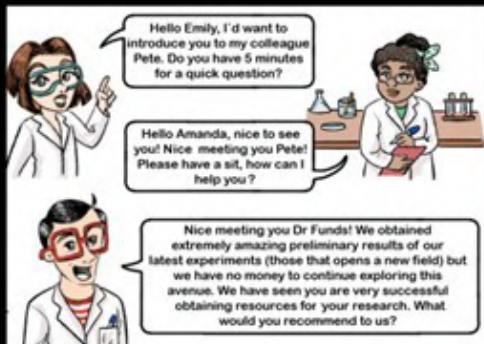
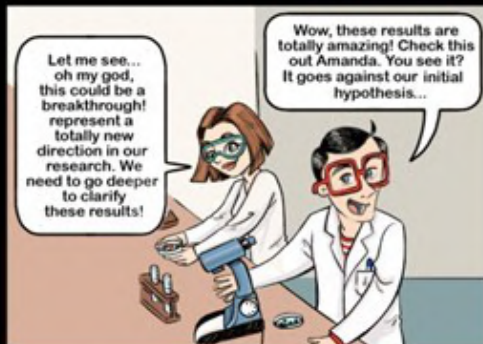


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# WHAT'S HER SECRET?





# NanoSpain Conf 2023

April 25 - 28, 2023 • Tarragona (Spain)

On behalf of the Organizing Committee, we take great pleasure in welcoming you to Tarragona (Spain) for the 20th edition of the NanoSpain International Conference.

Consolidated as a reference meeting of Nanoscience and Nanotechnology (N&N) in Spain, the NanoSpain2023 conference is not limited to a conventional presentation of ideas or results, but seeks to deepen the common themes among the participants, also serving as a link between industry and researchers. Over the past years, NanoSpain conference became more and more multidisciplinary and 2023 won't be an exception; covering a broad range of current research in Nanoscience and Nanotechnology.

Since 2004, year the event was launched, NanoSpain conference series aims to agglutinate and coordinate the efforts made in the field of Nanoscience & Nanotechnology by Spanish groups from universities, research institutes and companies.

NanoSpain2023 will offer a multitude of renowned international Keynote and Invited speakers, contributed talks, posters and a commercial exhibition. In addition, an industrial forum will be organized in collaboration with the COST Netpore network on Porous Semiconductors and oxides to promote constructive dialogue between business and public leaders and put specific emphasis on the technologies and applications in the Nanotechnology sector.

We would like to thank all participants, speakers, sponsors and exhibitors that joined us this year. Finally, thanks must be directed to the staff of all organizing Institutions making this event a reality.

*The Organising Committee*

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E20018 Donostia / San Sebastián  
Gipuzkoa, Spain

## ORGANISERS



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Chemical Physics of Complex Materials



Electronic Properties at the Nanoscale



Polymers and Soft matter



Photonics

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- **30 different nationalities** working together
- **70 international and local research projects** in active
- **170 annual publications** in top journals

## Education

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- **PhD Programme** Physics of Nanostructures and Advanced Materials
- **Master** in Nanoscience
- **Scholarship**

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The Donostia International Physics Center Foundation (DIPC - [dipc.ehu.es](http://dipc.ehu.es)) was created in 1999, the fruit of institutional collaboration between the Departments of Education and Industry of the Basque government, the University of the Basque Country, the Diputación Foral de Guipúzcoa, the San Sebastián City Hall, the Kutxa of Guipúzcoa and San Sebastián.

The DIPC was created as an intellectual centre whose main aim is to promote and catalyse the development of basic research and basic research oriented towards material science to reach the highest level. Since its creation, the DIPC has been an open institution, linked to the University of the Basque Country, serving as a platform for the internationalising of basic science in the Basque Country in the field of materials.

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## OTHER SPONSORS



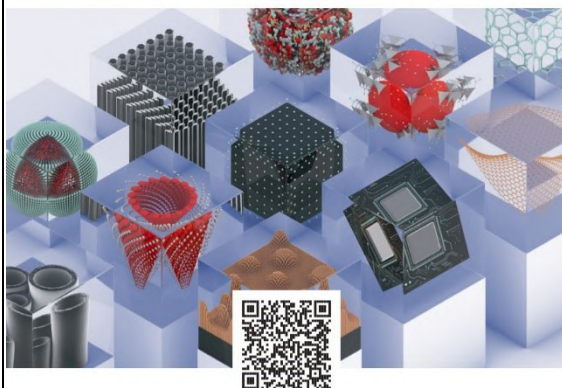
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## PARTNERS



The NETPORE COST Action will create an international network of world-class researchers and stakeholders to promote joint ideas and initiatives aiming to bridge the gap between fundamental developments and practical applications of technologies based on porous semiconductors and oxides

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The NETPORE COST Action will create an international network of world-class researchers and stakeholders to promote joint ideas and initiatives aiming to bridge the gap between fundamental developments and practical applications of technologies based on porous semiconductors and oxides.

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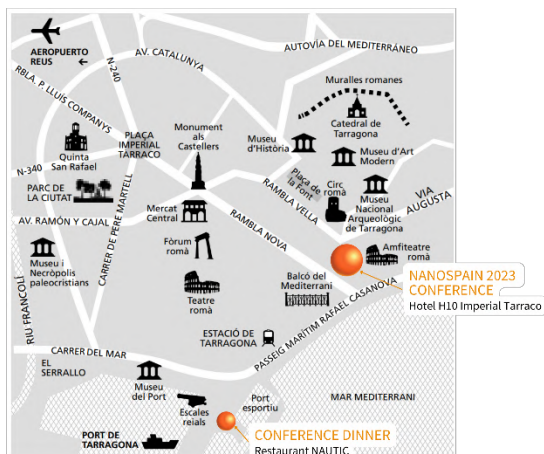
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## GENERAL INFO

<b>FREE WIFI</b>	WiFi: H10Salones / Password: SalasH10
<b>EXHIBITION &amp; POSTER AREA</b>	Forum
<b>COFFEE BREAKS</b>	Check the program online for timetables Location: Forum
<b>COCKTAIL LUNCH</b>	Offered by NanoSpain2023 organisers Tuesday April 25, 13:30-14:30 Thursday April 27, 13:30-14:30 Location: Exhibition & Poster Area
<b>CONFERENCE DINNER*</b>	Wednesday April 26, 21:00 <b>Restaurant NAUTIC</b> Edifici Nautic, Moll de Llevant, S/N 43004 Tarragona

\*Conference dinner NOT included in Exhibition pass. If you wish to attend, contact the organisers at the registration desk.



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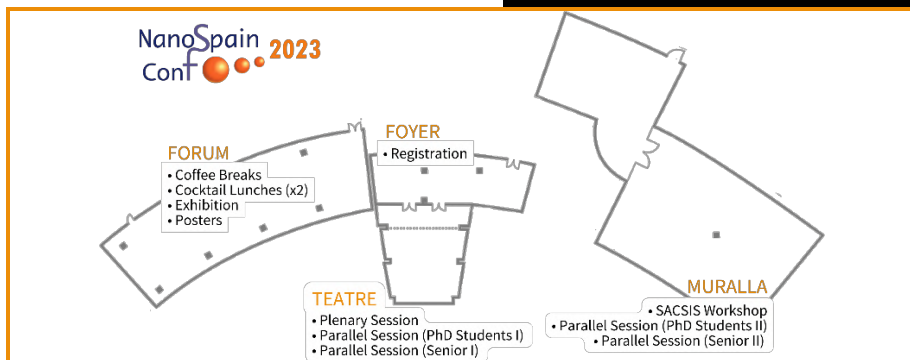
## ABSTRACTS BOOK

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## AGENDA & LOCATION



### Tuesday – April 25

	Room	Time
Registration	Foyer Teatre	08:00-08:45
Opening Ceremony	Teatre	08:45-09:00
NanoSpain2023 Plenary Session	Teatre	09:00-19:05
Poster Session I	Forum	14:30-15:00
Coffee Breaks, Exhibition & Poster Sessions	Forum	-
Cocktail Lunch (offered by the organisers)	Forum	13:30-14:30
Poster session - Exhibition	Forum	13:30-14:30

### Wednesday – April 26

	Room	Time
NanoSpain2023 Plenary Session	Teatre	09:00-19:00
"European Opportunities for postdoctoral Research" SACSIS Workshop	Muralla	09:00-10:30
Coffee Breaks, Exhibition & Poster Sessions	Forum	-
Conference dinner	Restaurant NAUTIC	21:00

### Thursday – April 27

	Room	Time
NanoSpain2023 Plenary Session	Teatre	09:00-13:30
Poster Sessions II	Forum	14:30-15:00
PARALLEL SESSION (PhD Students I) Nanomaterials	Teatre	15:00-16:40
PARALLEL SESSION (PhD Students II) Graphene/nanotubes, Nanobiotechnology & Simulation	Muralla	15:00-16:40
PARALLEL SESSION (Senior I)	Teatre	17:30-18:15
PARALLEL SESSION (Senior II)	Muralla	17:30-18:30
Coffee Breaks, Exhibition & Poster Sessions	Forum	-
Cocktail Lunch (offered by the organizers). Poster Session - Exhibition	Forum	13:30-14:30

### Friday – April 28

	Room	Time
NanoSpain2023 Plenary Session	Teatre	09:00-16:40
NanoSpain2023 Closing remarks	Teatre	16:40



# NETPORE

Network on porous  
semiconductors and oxides



## KEYWORDS

Porous Semiconductors  
Nanopores, Mesopores,  
Macropores  
Smart Functional Surfaces



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## Extreme Nanocavity-Enhanced Molecular Spectroscopy

Javier Aizpurua

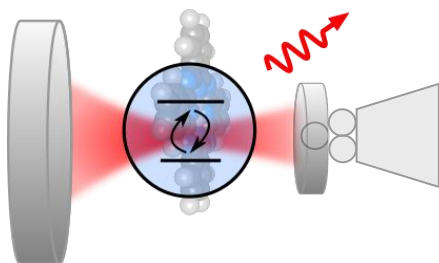
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A plasmonic nanogap is a superb configuration to explore the interplay between light and matter. Light scattered off, or emitted from a nanogap carries the information of the surrounding electromagnetic environment with it. This situation becomes even more appealing when a single molecule is located in such a plasmonic cavity or in its proximity, with the molecule playing an active role either in the electromagnetic coupling with the nanocavity, or even participating in processes of charge injection and transfer, as revealed through cutting-edge molecular spectroscopy. In this talk, the process of interaction between a molecular emitter and a nanocavity will be addressed by means of different theoretical frameworks which involve aspects of condensed matter physics [1], quantum chemistry [2], and cavity-quantum electrodynamics [3]. A battery of methodologies to address the dynamics of electrons photo-emitted from nanogaps, ultra resolution in atomic-scale photoluminescence, or non-linear regimes in molecular optomechanics will be described, and many of the theoretical insights obtained will be interpreted in the context of state-of-the-art experimental results in nanocavity-enhanced molecular spectroscopy.

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### Figures



**Figure 1:** Molecular electronic excitation constituted by a two-level system, coupled to an optical picocavity constituted by an atomic protrusion at the tip of a scanning tunneling microscope over a surface. Light emission (depicted with a red arrow) is produced in such a picocavity, which allows for identifying atomically-resolved intramolecular intensity of light emission, Purcell effect, and Lamb shift.

## Atomic-layer approaches towards 'extremely thin' chalcogenide-based photovoltaics: A unique combination of advantages

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Atomic layer deposition (ALD) and variants of the technique are ideally suited to the generation of 'extremely thin absorber' (ETA) solar cells, in which three distinct semiconductors are combined as electron transport layer (SnO<sub>2</sub>, TiO<sub>2</sub>, ZnO), light absorption layer (Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>Se<sub>3</sub>), and hole transport layer (V<sub>2</sub>O<sub>5</sub> or spin-coated organics). We have demonstrated six main advantages.

(1) ALD can deliver a material quality significantly improved with respect to solution processing techniques, with crystals of 10 µm lateral size obtained in planar films of 50 nm thickness.

(2) It enables the experimentalist to vary the thickness of layers within the semiconductor stack systematically and optimize the geometric parameters for overall energy conversion efficiency.

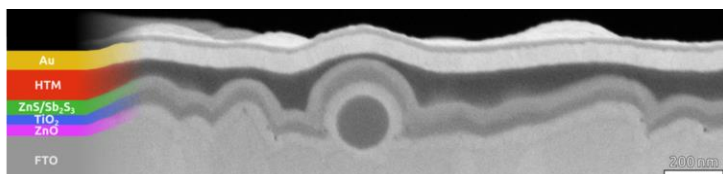
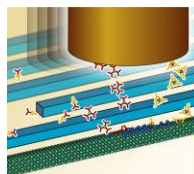
(3) It offers the opportunity to engineer interfaces with the use of interfacial layers providing chemical or physical functions (adhesion layers, tunnel barriers) with extreme thickness sensitivity, on the length scale of 0.5 to 1.5 nm.

(4) It provides the capability, unique among the deposition techniques from the gas phase, to deliver conformal coatings of non-planar substrates. Parallel arrays of cylindrical p-i-n heterojunctions in a coaxial geometry allow for decoupling the path lengths for light absorption and charge separation. Ordered monolayers of nanospheres can be exploited to scatter light of near-bandgap energy, enhancing the conversion of light incident in the red spectral range and/or under oblique angle.

(5) Our extension of ALD to the use of precursors dissolved in the liquid phase, instead of classically delivered from the gas phase ('solution ALD' or sALD) expands the range of materials accessible by ALD. It also provides additional experimental tools to adjust the deposit's morphology, and it provides an inexpensive access to ALD.

(6) The recent invention of 'atomic-layer additive manufacturing' (ALAM) circumvents the limitations associated with traditional blanket layering methods. It opens the door to rapid prototyping approaches in the photovoltaics field that mirror the use of 3D printing in manufacturing.

In summary, each major material family exploited in photovoltaics has been associated with a certain set of processing techniques, and our research indicates that atomic-layer processing provides all ingredients required for the success of the group 5 chalcogenides and similar light absorbers.



## Manipulating nanotube mechanical resonators with single-electron tunneling

Adrian Bachtold

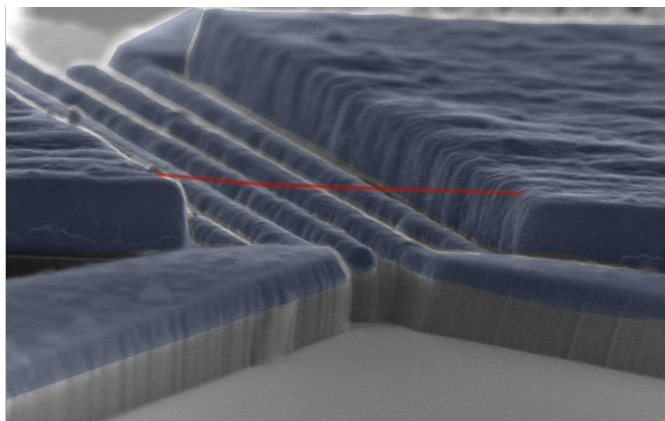
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Mechanics has historically played a pivotal role in science by providing the basis for classical physics. Today, with the advent of nanoscale mechanical devices combined with quantum electronic devices, we are witnessing a renaissance in the field of mechanics. Here, I will discuss our recent advances on resonators based on carbon nanotubes. In particular, single-electron tunneling enables coupling mechanical vibrations to electrons by a large amount in these systems. I will show how to use this coupling to create a nonlinear mechanical oscillator approaching the quantum regime, where the resulting quantum energy levels of the mechanical oscillator are no longer evenly spaced. Using mechanical nanotubes hosting multiple quantum dots, we expect that our approach may enable the realization of a mechanical qubit [1] and a quantum simulator of quantum matters featuring strong electron-phonon correlations [2,3].

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### Figures



**Figure 1:** Vibrating nanotube in red hosting a double-quantum dot



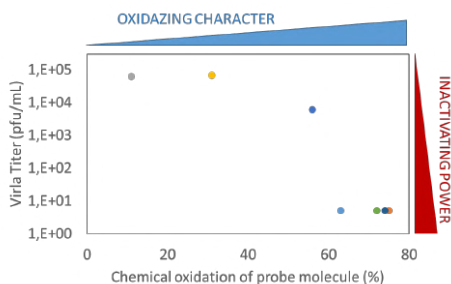
## Nanoparticle reactivity: a knife with two blades: from their health and safety risk to their use for indoor air microbiological remediation

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Lower respiratory tract infections represent the third leading cause of death in the world. Airborne transmission is the main propagation vector [1]. Virus-containing aerosols linger in air and remain infectious for hours. Current air virus inactivation methods are based on physical filtration, heat treatment, physical damage by UV-light or chemical damage by generation of reactive ions [2]. Their main problems relate to their efficacy, expensive materials, risk of infection during filter replacement, ocular and cutaneous UV-damage and the possibility of generating harmful secondary compounds. Our project develops catalytic filters, which will be placed in indoor air-cleaning device, inactivating viruses by oxidative stress through selectively heating the filter at mild temperatures.

Our experience in h2020 NanoInformaTIX project aiming at understanding the reactive bases of nanoparticle toxicity allowed us to predict environmental health and safety of nanomaterials [3], understanding nanomaterials reactivity. Among these, we have developed acellular oxidative stress assays to correlate with adverse outcome effect. Based on oxidative damage, such a knowledge can in turn be used to remediate indoor virus and bacteria by catalytic filters. To facilitate pre-screening, our acellular assay has been adapted and developed to evaluate the oxidative potential catalytic systems; it uses probe organic reactions. Acellular test are benchmarked vs. virus inactivation by plaque assays using virus in solution as first approach for inactivating power determination. Human coronavirus (HCoV-229E), severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) and rhinovirus (HRV-14).



**Figure 1:** Correlation between the catalyst oxidizing character and virus inactivation power.

The oxidative potential of different filters was evaluated and correlated with its potential to inactivate HCoV-229E virus at 37 °C and 1 h (Figure 1). The figure illustrates how the acellular assay can be used for a preliminary screening of catalytic materials.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814426 (NanoInformaTIX), CSIC PTI+ Salud Global Nextgeneration EU and CaixaFoundation HR22-00813 grant.

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## Implantable and bioresorbable chemical sensors for in-vivo tracking of clinical/diagnostic markers

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Imagine your doctor could slip a miniaturized sensing system under your skin and use it to continuously monitor the concentration of almost any molecule in real-time as it circulates through your peripheral blood. This would revolutionize many areas of diagnostics, enabling individualized reports on both disease progression and drug efficacy to be achieved continuously, in real-time. Imagine the sensing system implanted under your skin to communicate with your mobile phone (wireless communication) to transfer the clinically relevant data (biomarker or drug concentration) directly to your doctor. This would impact the way we diagnose diseases and monitor drug efficacy, currently based on single-moment-in-time tests, enabling personal, timely, and effective medical feedback (real-time personalized medicine). Finally, imagine the biochemical sensor in your body is resorbed upon a click, once you don't need it anymore. This would eliminate any need for sensor retrieval, avoiding risks connected to surgery and providing a risk-free "red button" to destroy it, in case issues will occur (e.g., end of the therapeutic process, inflammation, malfunctioning).

In this lecture, cutting-edge research on the use of bioresorbable nanostructured materials for the development of implantable bioresorbable sensors for analytes of clinical interest (e.g., drugs, biomarkers, ions) in-vivo, in-situ, and in real time that completely dissolve with biologically benign by-products after use will be reviewed and discussed.

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## Direct translocation through lipid bilayers: design challenges and solutions

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### Abstract

The development of nanomaterials that are capable of crossing lipid bilayers presents a significant challenge in the field of nanotechnology. To overcome this barrier, a diverse range of shapes, sizes, and surface coatings have been employed in the design of nanomaterials. The potential barrier for nano-objects to cross the lipid bilayer by thermal motion is too high for objects with a size greater than 5 nm. It is generally accepted that small hydrophobic nanoparticles are covered by the lipid bilayer and accumulate in the bilayer core, while nanoparticles larger than 5 nm can only penetrate cells through slow, energy-dependent processes such as endocytosis, which lasts for several minutes.

Here, we present several examples demonstrating how physico-chemical properties of nanoparticles can impact their ability to translocate passively through the lipid bilayer. In one case, variation of the hydrophobicity of nanoparticles induced reversible destabilization of the bilayer structure, leading to enhanced permeability for water and small solutes. In the other example, we show that lipid-covered hydrophobic nanoparticles can translocate through lipid membranes by direct penetration within milliseconds. Our results reveal that nanoparticles with diameters smaller than 5 nm remain trapped in the bilayer, while nanoparticles larger than 5 nm insert into the bilayer, opening transient pores in the bilayer. Another example demonstrates how cholesterol present in a lipid membrane can facilitate the translocation of nano-objects. A new type of nanodomain was discovered around ultra-short carbon nanotubes (USCNTs) in a two-component lipid bilayer containing cholesterol. This nanodomain weakens the attachment between USCNTs and the lipid bilayer, leading to detachment through pore formation, suggesting the role of cholesterol in the function of membrane ion channels and biophysics of membrane proteins with inserted nanoobjects.

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## Nanoneedles for Intracellular Sensing and Delivery

Ciro Chiappini

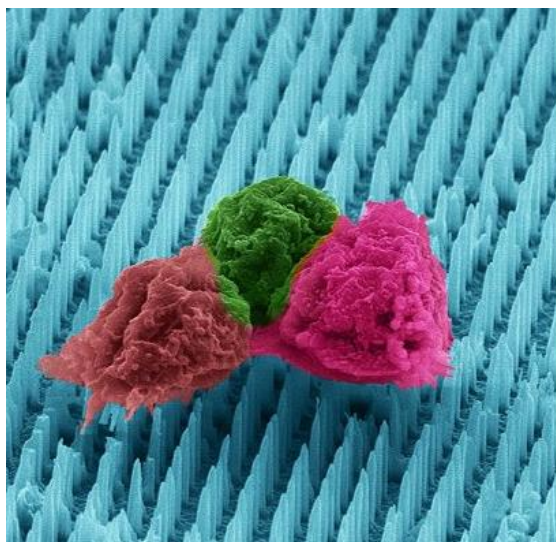
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Nanoneedles uniquely enable access to the cell with minimal perturbation, providing an appealing opportunity for nonimmunogenic delivery of labile biologicals and noninvasive sampling of intracellular material. This talk will outline our progresses in building a nanoneedle platform for topical delivery of nucleic acid therapies to epithelia and endothelia for regulation of gene expression and gene editing. It will further describe our recent advances in developing nanoneedles as a platform for spatial biology.

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### Figures



**Figure 1:** Scanning Electron Micrograph of three cells on nanoneedles.

## 2D Magnetic Heterostructures: from artificial magnets to smart molecular/2D heterostructures

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The controlled assembly of 2D materials in van der Waals heterostructures provides the opportunity to design unconventional materials with novel properties. Here I will illustrate this concept through two examples:

1) Artificial magnets obtained by creating a twisted 2D heterostructure formed by two ferromagnetic monolayers of CrSBr twisted by an angle of  $90^\circ$  [1]. Magneto-transport measurements in this new material show a multistep spin switching with the opening of hysteresis, which is absent in the pristine bilayer case (angle of  $0^\circ$ ) [2], as a consequence of the competition between the inter-layer exchange interactions (which favor an antiparallel orientation of both spin layers) and the local spin anisotropy and an external magnetic field applied along the easy magnetic axis  $b$  (which tend to orient the spins along this easy axis).

2) Smart molecular/2D heterostructures obtained by interfacing stimuli-responsive magnetic molecules with graphene or semiconducting transition metal dichalcogenides ( $\text{MoS}_2$  and  $\text{WSe}_2$ ). The aim is that of tuning the properties of the “all surface” 2D material *via* an active control of the hybrid interface. This concept will provide an entire new class of smart molecular/2D heterostructures, which may be at the origin of a novel generation of hybrid materials and devices of direct application in highly topical fields like electronics, spintronics and straintronics. As smart-molecular systems I will choose magnetic spin-crossover materials able to switch between two spin states upon the application of an external stimulus (temperature, light or pressure) [3]. This spin transition is always accompanied by a significant change of volume in the material (by ca. 10%), so it can generate strain in its surrounding. I will show that in these heterostructures the electronic properties of graphene and the optical photoluminescence of monolayers of semiconducting metal dichalcogenides can be switched by light or by varying the temperature due to the strain concomitant to the spin transition [4-6].

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## Interfacial liquid water on graphite, graphene, and 2D materials

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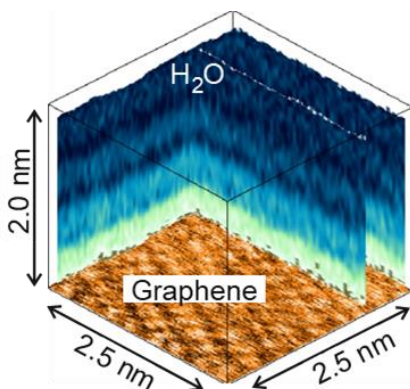
Solid-water interfaces have a prominent role in a variety of fields such as surface science, geochemistry, electrochemistry, energy storage or molecular and cell biology. Liquids near a solid surface form an interfacial layer where the molecular structure is different from that of the bulk. Yet the molecular-scale understanding of the interactions of liquid water with solid interfaces is unsatisfactory for the lack of high-spatial resolution methods. Here I will present an AFM-based method that provides atomic-scale resolution images of solid-liquid interfaces.

The presentation is divided in three sections. The first section is an introduction to the relevance of solid-liquid interfaces. The second section, presents the features and capabilities of 3D-AFM [1-3] to image with atomic resolution the **three-dimensional** interfacial structure of surfaces immersed in aqueous solutions. The third section reports the structure of interfacial water layers on different **2D materials** from graphene to a few layer MoS<sub>2</sub>; from hexagonal boron nitride to a few layer WSe<sub>2</sub>. Those interfaces are characterized by the existence of a 2 nm thick region above the solid surface where the liquid density oscillates [4-6]. The distances between adjacent layers for graphene, few-layer MoS<sub>2</sub>, h-BN and pentacene are ~0.50 nm. This value is larger than the one predicted and measured for water density oscillations (~0.30 nm). The experiments demonstrate that on extended **hydrophobic surfaces water** molecules are **expelled** from the vicinity of the surface and replaced by several molecular-size hydrophobic layers.

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**Figures 1:** Atomic-resolution 3D image of a graphene –water interface.



## Nanophotonics with Free Electrons

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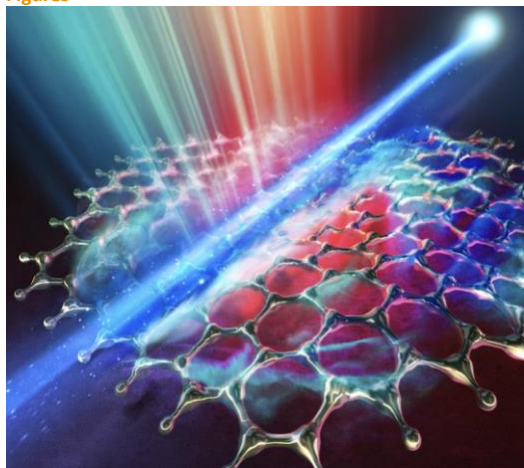
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Electron beams hold a unique position in the quantum photonic Lego because of their role both as a tool to unveil fundamental phenomena and as a resource for the excitation, probing, and control of quantum optical modes at the nanoscale. The ability to modulate the longitudinal and transverse wave function associated with free electrons has recently experienced an impressive boost thanks to the combination of new advances in electron sources/optics –in particular with the use of ultrafast light pulses– and the synthesis of femtosecond electron wave packets. In this talk, we overview key concepts describing the interaction between free electrons, light, and photonic nanostructures, making emphasis on quantum aspects and exploring several exciting challenges and emerging opportunities. In particular, we discuss potential applications in noninvasive spectroscopy and microscopy, sampling of the nonlinear optical response at the nanoscale, manipulation of the density matrices associated with free electrons and confined optical modes, optical modulation of free electrons for the generation of sub-nanometer/sub-femtosecond electron pulses, and improved schemes for electron-driven localized light source operating over a wide range of spectral ranges.

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### Figures



**Figure 1:** Illustration of a free electron interacting with a confined optical mode and procuding cathodoluminescence, as well as a signal encoded in the transmitted electron spectrum. In the reversed process, under illumination of the optical mode by ultrafast laser pulses, the wave function of the electron can be shaped and its duration compressed down to the attosecond range. Image reproduced from Ref. [1].

## Nanostructured Silicon – a Versatile Host Material Applicable as Biomedical, Magnetic and Optical Material

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This presentation deals with the utilization of nanostructured silicon for deposition of various metals, especially magnetic ones, within the pores/tubes. The novel magnetic properties of the semiconducting/magnetic composites which arise due to the nanoscopic size of the used materials are investigated with respect to biomedical and magnetic on-chip applications.

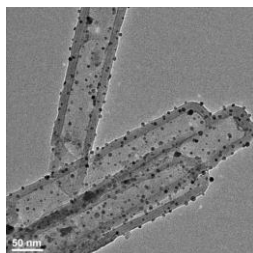
One of the key topics is the deposition of hard and soft magnetic materials within the nanostructures, aiming in the fabrication of arrays of permanent nanomagnets is shown [1]. Here the investigation of the magnetic behavior of bi-metal nanostructures within nanostructured silicon (figure 1) with the aim to exploit the magnetic properties of both metals and gain control of the exchange coupling between the two metals especially with respect to their volume ratio is discussed. Furthermore, a variation of the structure size and the proximity of the metal deposits modify the exchange coupling and thus the energy product. Nanocomposite systems with an energy product as high as possible should be achieved to give rise to on-chip applications using permanent nanomagnets, especially arranged in arrays.

A further issue, luminescent porous silicon loaded with magnetic metals to enhance the photoluminescence, is addressed with the final aim to influence/control the optical properties by a magnetic field. The metal deposits affect the optical properties but also give rise to specific magnetic behavior [2]. Due to the metal filling of the porous silicon the photoluminescence is blue-shifted and furthermore an increase of the intensity is observed. The influence of the magnetic metal filling on the optical properties (photoluminescence, decay time) is discussed and the magnetic characterization of the nanocomposites is presented.

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### Figures



**Figure 2:** SiNTs loaded with FePt nanoparticles with an average size of 5 nm.

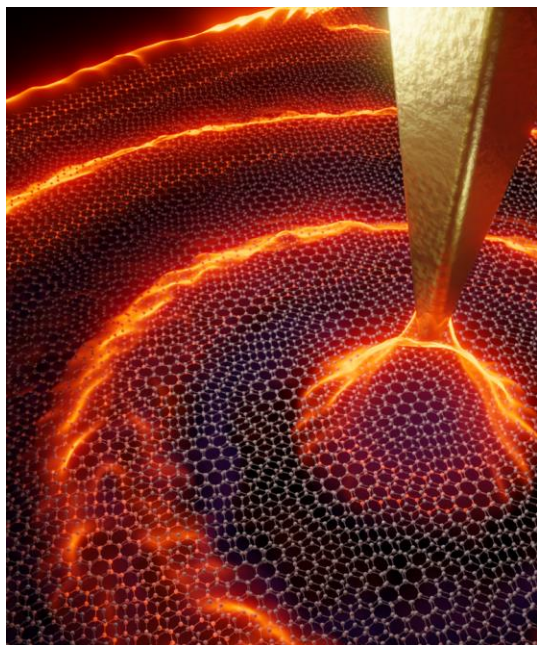
## Nanocavities, nano-imaging, and quantum technologies with twisted and stacked 2D materials

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Two-dimensional (2D) materials have extraordinary potential to control light and light-matter interactions on an atomic scale. Recently, twisted 2D materials have drawn considerable attention due to their capability of inducing moiré superlattices and the discovery electronic correlated phases. Various nanoscale optoelectronic probing scheme, utilizing infrared and terahertz radiation, are presented, revealing the materials topology, photoconversion, interaction effects and even single photon detection capabilities. Furthermore, by probing modulated 2D materials on the nanoscale, record-small nanoscale polaritonic cavities are revealed, as well as the formation of nanoscale hypercrystals, exhibiting negative refraction and topological interface states

### Figures



## Plasmonic Chirality in Individual and Assembled Nanoparticles

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The field of chirality has seen a strong rejuvenation due to the observation of nanoscale chirality in plasmonic nanoparticles [1,2]. This lecture will highlight recent advances in the field of plasmonic chirality, including novel methods for the synthesis of optically active plasmonic nanomaterials. Although much research in this field has been related to chiral nanostructures formed by the directed self-assembly of gold nanorods on various chiral templates, recent work has demonstrated the possibility of employing the well-known seeded-growth method to endow colloidal nanoparticles with chiral features. Recently developed approaches will be introduced, comprising either the use of chiral amino acids [3] or the self-organization of surfactant micelles into chiral structures on nanoparticle seeds [4]. These concepts open up a wide range of possibilities, by playing around with the variety of potential chiral co-surfactants, seed morphologies and metal compositions, which have been studied in the context of the seeded growth of metal nanoparticles. We demonstrate that the addition of chiral additives leads to different types of chiral features in the overgrown nanoparticles, resulting in high optical handedness, which can be tuned through the visible and the near IR [4,5].

On a different direction, chiral nanostructures can be formed by using biological templates, proteins in particular. Gold nanorods were found to self-assemble on amyloid fibers, following their double-helical structure. We propose that plasmon-enhanced chiral signals have great potential for use in the detection and therapy of neurodegenerative disorders [6].

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## Recent Advancements in Development of Anodic TiO<sub>2</sub> Nanotube Layers

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Self-organized TiO<sub>2</sub> nanotubes arrays, formed by electrochemical anodization of Ti, have attracted tremendous scientific and technological attention, due to their remarkable properties such as the tunability of dimensions, their directionality, high surface area, low density, and ability to absorb significant amount of incident light [1,2].

The most widely used electrolyte for the synthesis of TiO<sub>2</sub> nanotube layers is based on ethylene glycol containing small amounts of water and fluoride ions. However, nanotubes prepared in these electrolytes present a double-walled structure, with the outer wall consisting of almost pure TiO<sub>2</sub> and the inner wall consisting of TiO<sub>2</sub> contaminated with carbon and fluoride species [3,4]. In the recent years, the selective etching of the inner nanotube wall on Ti layer enabled synthesis of single-wall nanotubes that showed a superior photo-electrochemical performance compared to their double-walled counterparts [5]. An extensive etching enabled also the synthesis of single tube powders, which could be effectively decorated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles to act as magnetically guidable photocatalyst [6,7].

In addition, the area that can be anodized was significantly upscaled to dozens of cm<sup>2</sup>, and benefit of such large area TiO<sub>2</sub> nanotube layers have been founds in very efficient gas and liquid phase photocatalysis [8].

The presentation will review of all these advancements in the nanotube morphologies, anodizable areas as well as nanotube chemistries and their impact on applications, with focus on the photocatalytic degradation in the gas and liquid phase and several other biological and electrochemical applications. In particular, we will discuss, how the annealing temperature of single nanotubes influences their photocatalytic performance [7], how the wall thickness of the single wall nanotubes can be optimized for the best performance [9], how to tune the color of the tubes, etc. Experimental details and photocatalytic results will be presented and discussed.

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## Nanocomposite peptide hydrogels: from nanocarbon to gold nanoparticles

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Nanocomposite hydrogels are attractive soft materials with multifunctional applications. Our group has expertise on the design of minimalistic, heterochiral peptides that feature D- and L-amino acids at specific positions to modulate their self-assembling behaviour into functional nanostructures [1-3]. Recently, we became interested in introducing additional features by developing supramolecular nanocomposites with other types of nanosized components, including nanocages for chemical separation [3-4], carbon nanomaterials [6-8], and gold nanoparticles prepared in situ using the peptide as mild reductant. In this lecture, nanomorphological and supramolecular effects will be discussed to outline key lessons learnt for the future development of nanocomposites that could find a variety of applications, from sensing to therapy [9-10], and environmental remediation [3,5].

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### Figures

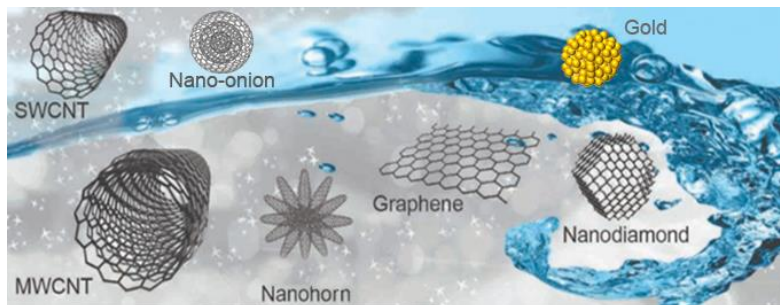


Figure 1: Nanocomposite hydrogels with various carbon nanostructures and gold nanoparticles.

# Importance of Three-Dimensional Nanowire Networks in Optics, Magnetism, and Energy Harvesting

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## Abstract

Three-dimensional nanowire networks are structures made of interconnected nanowires that form a three-dimensional mesh. They have the potential to revolutionize areas such as magnetism (generating materials with tailor magnetic behavior), electronics (generating new transistors and sensors), energy harvesting (since new phenomenology appear at nanoscale), energy storage (improving the performance of batteries and supercapacitors, making them more efficient and durable), or biomedical devices (such as new biosensors). These three-dimensional nanowire networks can be generated in areas from mm<sup>2</sup> up to ~m<sup>2</sup>. The junctions between adjacent nanowires render excellent mechanical stability. So, the nanowire network can be free-standing after elimination of the template or the substrate in which they have been grown. The wires mechanically support each other, and in case individual wires break, electrical or thermal transport can still occur via alternative nanowire interconnections.

By means of several examples, I will illustrate how 3D nanowire networks combine the advantages and ease of handling of macroscopic samples with the size-dependent properties of nanowires. For instance, they can be used to create high-performance transistors that are smaller than 10 nm. They can also be used to create biosensors that are highly sensitive to glucose. Furthermore, they can be used to create high-capacity lithium-ion batteries that are more efficient and durable than conventional batteries.

In this keynote, I will show some examples of Three-dimensional nanowires networks to generate materials with tailor magnetic behavior that could have important applications in fields such as data storage and spintronics. Or, to create flexible Bragg reflectors that could have applications in optics and photonics. Or, to eliminate phonon transport in thermoelectric metamaterials, which could have important applications in thermoelectric devices.

## Magnetic order in a coherent two-dimensional Kondo lattice

Wen Wan<sup>1</sup>, Rishav Harsh<sup>1</sup>, Antonella Meninno<sup>2</sup>, Paul Dreher<sup>1</sup>, Sandra Sajan<sup>1</sup>, Ion Errea<sup>1,2</sup>,  
Fernando de Juan<sup>1,3</sup> and **Miguel M. Ugeda**<sup>\*,1,2,3</sup>

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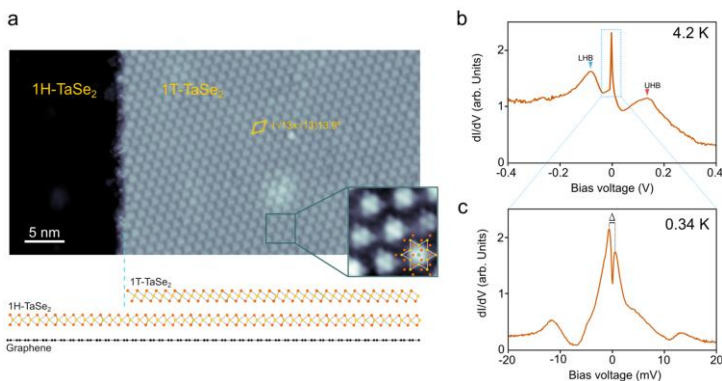
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Kondo lattices are ideal testbeds for the exploration of heavy-fermion quantum phases of matter. While our understanding of Kondo lattices has traditionally relied on complex bulk *f*-electron systems, transition metal dichalcogenide heterobilayers have recently emerged as simple, accessible and tunable 2D Kondo lattice platforms where, however, their ground state remains to be established. Here we present evidence of coherent magnetism in the 1T/1H-TaSe<sub>2</sub> heterobilayer by means of scanning tunneling microscopy/spectroscopy at 340 mK. Our measurements reveal the existence of two symmetric electronic resonances around the Fermi energy, a hallmark of coherence in the spin lattice. Spectroscopic imaging locates both resonances at the central Ta atom of the charge density wave of the 1T phase, where the localized magnetic moment is held. Furthermore, the evolution of the electronic structure with the magnetic field reveals a non-linear increase of the energy separation between the electronic resonances. Aided by *ab initio* and auxiliary-fermion mean-field calculations, we demonstrate that this behavior is inconsistent with a fully screened Kondo lattice, and originates instead from a ground state with magnetic order mediated by conduction electrons. The manifestation of magnetic coherence in TMD-based 2D Kondo lattices enables the exploration of magnetic quantum criticality, Kondo breakdown transitions and unconventional superconductivity in the strict two-dimensional limit.

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### Figures

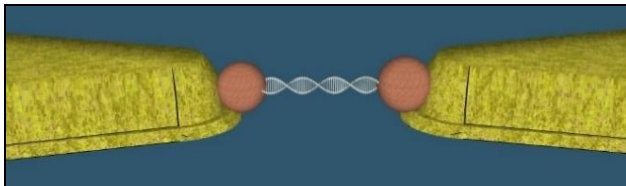


**Figure 1: Atomic and electronic structure of the 1T-TaSe<sub>2</sub>/1H-TaSe<sub>2</sub> heterobilayer.** **a**, Large-scale STM image of a monolayer of 1T-TaSe<sub>2</sub> on monolayer 1H-TaSe<sub>2</sub> grown on BLG/SiC(0001). Below a sketch of the vertical arrangement of the atomic layer is shown. The inset shows a high-resolution STM image of the CDW supercell, where a sketch of the CDW Star of David is overlaid. **b**, Typical dI/dV spectrum taken on the 1T/1H heterostructure at 4.2 K. The position of the lower (upper) Hubbard band is indicated. **c**, Low-bias dI/dV spectrum acquired on the 1T/1H heterostructure at our base temperature of 0.34 K showing the emergence of two peaks, a hallmark of quantum coherence.

## Molecular Electronics with DNA towards Detection of Nucleic Acids

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The DNA double-strand recognition, as well as the ability to manipulate its structure open a multitude of ways to make DNA useful for molecular electronics. We recently reported a breakthrough in measuring charge transport in DNA (Nature Nanotechnology 2020) in a special configuration. This finding is of great importance by itself for understanding electricity in DNA in particular, and for molecular electronics in general. However, it also paves the way for the design of new ultra-sensitive detectors for DNA and RNA. Addressing these challenges is at the heart of early detection of cancer, pathogens, emergency medicine as well as for pandemics like the COVID-19.

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## Atomically precise devices: the challenge of nanofabrication

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Our research group is committed to applying the ideas of atomically perfect material synthesis to the resolution of real issues in many technological and industrial fields. Our method is not restricted to the creation of materials from the bottom up; it also requires a thorough comprehension of the atomic-scale interactions that regulate the behaviour of mesoscopically complex systems. One of our ongoing research projects investigates the viability of Ferromagnetic Insulators/Superconductor heterostructures as a novel platform for future quantum advancements.

To attain this objective, we must first control the structural, chemical, electrical, and magnetic properties of the layer-by-layer materials with extreme precision. Then, we use these materials to create devices and investigate the relationship between their properties and the mesoscopic response, such as transport and thermoelectricity. Specifically, we are examining heterostructures that combine thin layers of EuS in contact with Al, as well as evaluating the usage of all 2D devices that mix NbSe<sub>2</sub> superconductors with 2D ferromagnetic insulators such as Transition metal dihalides.

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### Figures

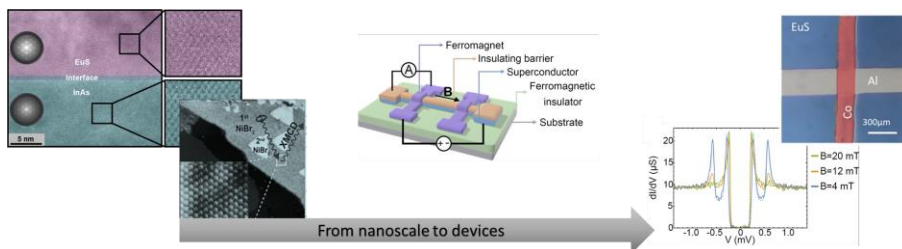


Figure 1: Schematic representation of fabrication of atomically precise devices.



## Re-Etched anodized porous silicon: from drug delivery to optical applications

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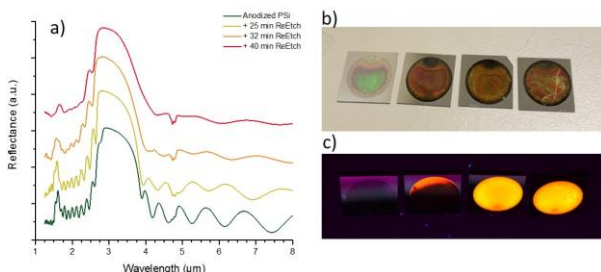
Hierarchically nanostructured silicon can be produced by regenerative electroless etching [1] (ReEtching) of initially anodized porous silicon (RAPSi) [2]. The ReEtched material retains its characteristic anodized mesopores, upon which tortuous 2–4 nm pores have been introduced throughout the pore walls. The walls become sufficiently narrow to support quantum-confined crystallites that are brightly photoluminescent. The regenerative nature of the ReEtching process also provides control over the emission color of the photoluminescence. Mechanical milling and hydrosilylation of this still hydrogen terminated PSi powder with undecylenic acid can be used to produce hydrolytically stable nanoparticles of ~220 nm in diameter. The nanoparticles exhibit robust and bright luminescence that can be excited with either a single ultraviolet/visible photon or even with two near infrared (NIR) photons. The application of two-photon fluorescence imaging for obtaining higher spatial resolution, contrast and the suppression of tissue autofluorescence has received significant interest. This feature is highly beneficial, not only for *in vitro* cell studies or for histopathological studies of tissue, but due to the better tissue penetration of NIR photons, it can also be applied in *in vivo* time-gated fluorescence imaging of small animals as well [3].

In addition to the significantly larger specific surface area of RAPSi, which can reach over 1000 m<sup>2</sup>/g, an important feature when considering drug loading and release, there is also another, recently discovered effect of ReEtching of anodized PSi. ReEtching of anodized PSi Bragg reflector multilayer structure suppresses the sidelobes, characteristic for Bragg mirrors in a very similar fashion as in rugate filters when produced with e.g. an apodization function or index matched layers (Figure 1). Technically, ReEtching of anodized Bragg reflectors is simpler than direct rugate filter fabrication, and this offers more freedom to adjust e.g., the reflection bandwidth. Moreover, the reflectors can be made to exhibit similar luminescence properties as the nanoparticles.

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### Figures



**Figure 1:** a) Reflection band changes during the ReEtching. b) The reflectors under normal illumination and c) under UV excitation (365 nm).

## Molecular solar cells: From Dyes to Hybrid Semiconductors

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During my lecture I will present our latest results<sup>1,2</sup> on the characterization of different type of solar cells from DSSC and OPV to MAPI using advanced photo-induced time resolved techniques. Using PICE (Photo-induced charge extraction), PIT-PV (Photo-induced Transient PhotoVoltage) and other techniques, we have been able to distinguish between capacitive electronic charge, and a larger amount of charge due to the intrinsic properties of the perovskite material. Moreover, the results allow us to compare different materials, used as hole transport materials (HTM), and the relationship between their HOMO and LUMO energy levels, the solar cell efficiency and the charge losses due to interfacial charge recombination processes occurring at the device under illumination. These techniques and the measurements carried out are key to understand the device function and improve further the efficiency and stability on perovskite MAPI based solar cells (Figure 1).

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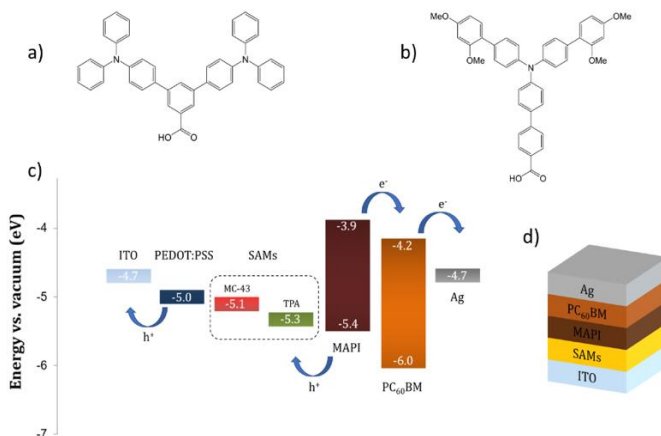


Figure 1. Use of self-assembled molecules as selective contacts in methyl ammonium lead iodide (MAPI) perovskite solar cells.

## Nanobots as a new nanotherapeutic modality in biomedicine

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One of the dreams in nanotechnology is to engineer small vehicles and machines, called here nanobots, which can eventually be applied in vivo for medical purposes. Yet, reaching that fascinating goal is not a trivial thing and several challenges need to be addressed. First, researchers need to incorporate efficient but also bio-friendly propulsion mechanisms into the nanobots. Our strategy comprises the use of biocatalysts such enzymes for converting biologically available fuels into a propulsive force. Secondly, nanoparticles' chassis should be generally recognized as safe (GRAS) material, biocompatible and/or biodegradable.

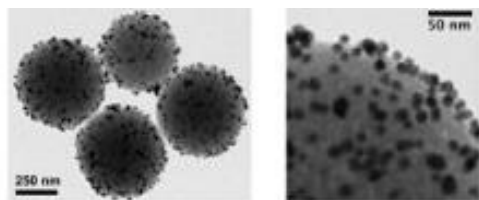
In my talk, I will present how we bioengineer hybrid nanobots combining the best from the two worlds: biology (enzymes) and (nano)technology (nano- micro-particles, Figure 1) providing swimming capabilities, biocompatibility, imaging, multifunctionality and actuation.

Besides the understanding of fundamental aspects (1), and controlling the performance of micro-nanobots (2) I will present some of the proof-of-concept applications of biocompatible nanobots such as the efficient transport of drugs into cancer cells (3) and 3D spheroids (4), sensing capabilities (5), anti-bactericidal applications (6) and the use of molecular imaging techniques like PET-CT (7) or Photoacoustic (8) for the tracking and localization of swarms of nanobots both in vitro and in vivo in confined spaces like mice bladder.

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### Figures



**Figure 1:** Mesoporous silica nanoparticles decorated with gold-nanoparticles used as basic architecture for nanobots.

## New palette of smart materials for soft robotics applications

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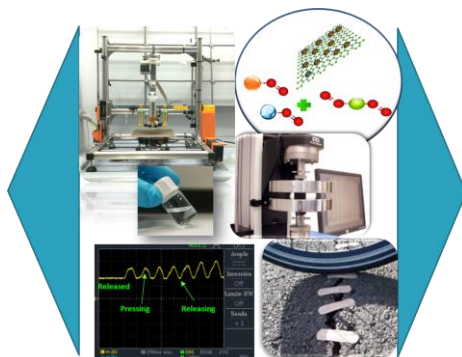
The synthesis of different hydrophilic polymeric networks, by in situ radical polymerisation in the presence of graphene derivatives, results in soft three-dimensional structures. The role of the nanomaterial within the polymeric network is mainly reinforcement (i.e. increased stiffness and toughness). However, we have shown that the presence of graphene can also enhance characteristics such as biocompatibility [1], sensing [2] or self-healing behaviour [3], giving rise to truly hybrid composites [4]. In addition, the ability of these materials to respond to different stimuli, such as electrical fields, and the possibility of preparation following 3D printing methodologies, opens the way to applications in soft robotics.[5]

These structures require 2D materials that are easily dispersible in water, and for this reason, sustainable mechanochemical methods developed in our laboratories have proven their utility for the preparation of the starting materials.[6]

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Figure



## Ferroelectricity in hexagonal boron nitride

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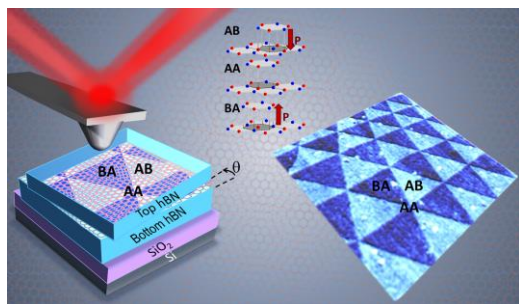
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Two-dimensional (2D) hexagonal boron nitride (hBN) is a wide-bandgap van der Waals crystal with a unique combination of properties, including a honeycomb lattice very close to that of graphene, exceptional strength, high oxidation resistance at high temperatures and optical functionalities [1]. As a result, it has become a ubiquitous material for the fabrication of van der Waals heterostructures [2]. Like many Group III nitride materials, its covalent bonds are highly polar, presenting the possibility of piezoelectricity [3] and spontaneous polarizations in the correct crystal configurations. In this talk, I will present the occurrence of spontaneous out-of-plane polarization forming ferroelectric-like domains at anomalously stacked hBN interfaces [4]. We have observed these effects using atomic force microscopy (AFM) electrical modes, namely electrostatic (EFM) and Kelvin Probe (KPFM) Force Microscopy, in combination with detailed modelling of in-plane deformation profiles and interface relaxation. Both the in-plane piezoelectricity and the out-of-plane ferroelectricity presented here open up interesting possibilities for precise control of device properties. The experimental approach used here also shows a way to investigate the polarization properties of other materials at the nanoscale.

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### Figures



**Figure 1:** Ferroelectric-like domains in hBN

## Sizing plasmonic nanoparticles with Dark-Field Single Particle Spectrophotometry

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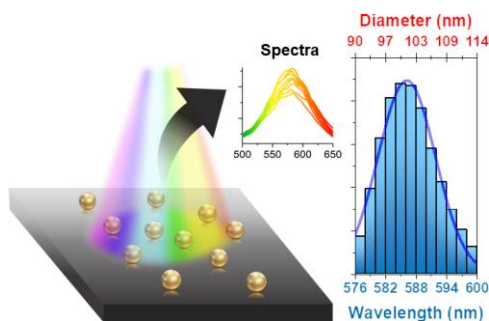
Plasmonic nanoparticles are widely used in scientific and industrial applications due to their unique optical properties. However, controlling the size and shape of large populations of nanoparticles remains a challenge, as variations in these properties can strongly influence their plasmonic response. Accurate characterisation of the morphological properties of nanoparticles is therefore crucial. In this context, a new optical method, called dark-field single-particle spectrophotometry (DF-SPS),<sup>[1]</sup> has been developed to measure individual particle sizes with nanometric accuracy in just a few minutes. The method features simple preparation, a simple experimental setup inspired by a custom optical microscope, and a measurement protocol that can be performed by untrained technicians.

A proof-of-concept study using thousands of spherical nanoparticles of different sizes showed that the method is highly accurate, with a variation of only 3% compared to the gold standard measurement technique of electron microscopy. In addition, the method has the potential to measure any geometry, including nanoshells and nanorods. Overall, the new method represents a significant advance in the synthesis and characterisation of plasmonic nanoparticles, with the potential to greatly improve the quality and consistency of nanoparticles used in various applications.

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### Figures



**Figure 1:** The DF-SPS technique involves characterizing the scattering signal of particles on a substrate, achieved by illuminating the substrate sequentially with light of different wavelengths (as depicted in the image). The resulting histogram shows the plasmonic maximum of thousands of 100 nm nominal size particles, which were converted into diameter measurements using the Mie theory.<sup>[2]</sup> The histogram data has been fitted to a Gaussian distribution, yielding an average size of  $101.6 \pm 2.8$  nm and a CV around 6%.

## Carbon-based Materials for Solar-driven Catalysis

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Carbon dots (CDs) and carbon nitrides (CN<sub>x</sub>s) are promising carbon-based materials that have garnered increasing interest as they are easy and inexpensive to synthesize, biocompatible, environmentally benign, water soluble, and display excellent photoluminescence and fluorescence, together with tunable optical properties.[1-3]

On the one hand, CDs are pseudospherical polydisperse nanoparticles (1-10 nm) that consist of a carbonaceous core stabilized by oxidized surface groups. We have applied them to produce solar fuels and chemicals. First, we deconvoluted the different sizes that form the bulk material. TEM and DLS confirm size-dependent separation and the monodisperse fractions show a size-dependent UV-vis and fluorescence spectroscopy response. A size-dependent effect on the photocatalytic H<sub>2</sub> evolution performance of the CDs in combination with a Ni cocatalyst has been demonstrated with a maximum activity at approximately 2-3 nm CD diameter. Then, for the first time, positively and negatively surface-functionalized CDs have been interfaced with the CO<sub>2</sub>-to-formate reducing enzyme formate dehydrogenase to study the enzyme-material interface during photocatalytic CO<sub>2</sub> reduction.[4] Finally, we show CDs for metal-free light-driven trifluoromethylation of aromatic compounds, including biological molecules, as well as cross-coupling of aldehydes, and a light-driven dual Ni/CDs photocatalytic system for photoredox catalysis.

On the other hand, CN<sub>x</sub>s are emerging organic semiconductors that have had an increasing interest in organic photocatalysis, due to their scalable synthesis, recyclability and robustness due to their heterogeneous nature. In this line, graphitic carbonitride (CN<sub>x</sub>), a polymeric material composed of heptazine units, has emerged as one of the most promising heterogeneous photocatalysts.[5] CN<sub>x</sub> has a broad absorption in the UV/Vis region and an optical band gap of approximately 2.7 eV, making it suitable for various photocatalytic applications.[6-7] In this context, we have developed a Ni doped mpg-CN<sub>x</sub> integrated heterogeneous photocatalysts that works as a Ni single-site photocatalyst for the cooperative photocatalytic C-O and C-N bond formation reactions.[8,9]

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## All-electrical spin control in low-symmetry materials

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### Abstract (Calibri 8)

The existence of the quantum spin Hall (QSH) insulator has boosted opportunities for spintronics and quantum metrology, given the ability of topologically protected states to convey spin information over long distances at ultralow dissipation rate. QSH is a manifestation of strong spin-orbit coupling. However, even in time-reversal symmetric systems, the lack of a spin conservation axis in QSH insulators allows backscattering effects for edge states, limiting their ballistic transport. In some situations, the emergence of a phenomenon known as persistent spin texture (PST) enforces spin conservation and favors long spin lifetimes even in the presence chemical disorder and structural imperfections. Such an effect is deeply rooted in the underlying symmetries of the system and opens promising prospects for spintronics when combined with the manifestation of dissipationless chiral edge states. The recent prediction and experimental observations of a PST-driven canted quantum spin Hall effect in low-symmetry monolayer WTe<sub>2</sub> provide new ingredient for the use of topological materials in spintronic applications.

This work reports on the possibility of a fully controllable variation of up to 90 degrees rotation of the spin polarization of chiral edge-states, dictating the canted QSH effect, while preserving spin conservation. By combining density functional theory (DFT) with tight-binding methods and quantum transport simulations, we show that the emerging PST can be continuously varied from in-plane to out-of-plane under electric fields below 0.1 V/nm, making this effect experimentally accessible. The experimental confirmation of such fully electrically tunable spin-polarized topological currents would establish a new milestone towards replacing magnetic components in spintronic devices and all-electric spin circuit architectures, as well as optimized resistance quantum standards.

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## Beyond graphene: how to synthesize hexagonal boron nitride crystals by chemical route

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Hexagonal boron nitride (hBN) occupies a special place in the vast world of two-dimensional (2D) materials due to its excellent thermal, chemical, mechanical, and dielectric properties. Whether used as a substrate or as an active layer, high-quality 2D hBN holds great promise for future research applications, especially for optoelectronic devices. However, it is now well established that the optical, electronic, and transport properties of these systems are highly dependent on the chemical purity and crystallinity of the hBN used, which in turn are highly dependent on the synthesis approach chosen. Vapor-phase processes, like chemical vapor deposition, can achieve large-scale coverage, but self-standing hBN crystals provide exfoliated nanosheets (BNNS) of unmatched purity and crystal quality which are still preferred for demanding applications.

In order to obtain high-quality, large-sized BNNSs, we propose a synthesis route based on the polymer-derived ceramics (PDCs) process [1]. PDCs consists of synthesizing a molecular precursor and then polycondensing it into an inorganic polymer that can be shaped before ceramization. This chemical route allows the elaboration of ceramics with adapted textural and structural properties, presenting specific shapes that cannot be easily obtained by conventional powder technology. By coupling PDCs to a sintering step, single crystals of hBN of a few millimeters were successfully obtained from a borazine precursor at a relatively low temperature [2]. The hBN obtained by this method shows a very high crystal quality attested by a Raman FWHM value of  $7.6 \text{ cm}^{-1}$ , one of the best reported in the literature [3]. BNNSs exfoliated from these crystals have been used to fabricate metal-hBN-metal capacitor devices to measure the dielectric constant and the breakdown electric field of hBN, which were found to be  $3.136$  and  $0.64 \text{ V.nm}^{-1}$  respectively [4], i.e very close to the theoretical values. Such functional measurements allow the assessment of the overall crystal quality. These BNNSs have also been used to encapsulate Transition Metal Dichalcogenides (TMDs) tested by optical spectroscopy. The photoluminescence widths of  $\text{WSe}_2$  and  $\text{MoSe}_2$  neutral exciton lines at 4K were measured within the 2-3 meV range [3] which is comparable to the results obtained with the highest quality hBN. All these results demonstrate that these BNNSs are relevant for future electronic and optoelectronic applications.

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## New nanomaterials for biomedical applications with focus on phototherapy

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Nanosized graphene oxide (GOn) is stable in aqueous dispersion, due to the oxygen functionalities on its surface, but possess low photothermal efficiency in NIR region. GOn total reduction originates reduced nanographene oxide (rGOn) that presents high NIR absorption, but poor water stability. In this work, we produced a never before reported reduced nanographene oxide (N-rGOn) by GOn photoreduction using light irradiation, yielding nanometric particles that preserve the original water stability, but acquire high light-to-heat conversion efficiency. GOn and New-rGOn presented mean particle sizes of  $170 \pm 81$  nm and  $188 \pm 99$  nm, respectively. 8 h of light irradiation allowed to obtain a N-rGOn stable for up 6 months in water, with a zeta potential of  $-32.3 \pm 1.3$  mV. N-rGOn water dispersions have shown to absorb NIR radiation, reaching  $57.2^\circ\text{C}$  ( $250\ \mu\text{g mL}^{-1}$ ) after 30 min of NIR irradiation. Chemical characterization of N-rGOn showed a decrease in the number of characteristic oxygen functional groups, confirming GOn suitable chemical modification. Furthermore, N-rGOn ( $150\text{--}250\ \mu\text{g mL}^{-1}$ ) has been proven not to have impact on human skin fibroblasts (HFF-1) cell viability, after 24 h of incubation. Finally, an innovative custom-built NIR LED-system has developed and validated for N-rGOn photothermal effect evaluation.

A general perspective on the work of our team will be presented, focusing on applications of graphene-based nanomaterials in phototherapy, immunotherapy and 3D-printing for tissue regeneration [1-3].

### Acknowledgements

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## MXenes in the world of the 2D-based hybrid nanomaterials

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### Abstract

Two-dimensional (2D) solids, such as graphene, transition metal dichalcogenides, and phyllosilicates belonging to the clay minerals family, are of increasing interest for the preparation of functional nanomaterials, including hybrids and bionanocomposites. Among 2D solids, an outstanding emerging group of transition metal carbides and carbonitrides termed MXenes, discovered in the last decade (1), are derived from ternary transition metal carbides and/or carbonitrides ( $M_{n+1}AX_n$ ,  $n = 1-3$ ) named "MAX phases" (1). MXenes are receiving enormous attention due to their physicochemical properties, in some aspects close to clay silicates but showing high electrical conductivity (1,2). In fact, they are also known as "conductive clays" (2), although in our view the use of "clays" to refer to MXenes should be avoided.

In this communication we will present a comparative study between layered clay minerals and MXenes, emphasizing aspects related to their structural, physical and chemical characteristics, with special emphasis on the ability of both types of 2D solids to act as host materials for the intercalation of various organic compounds, including polymers, thus giving rise to functional hybrids and nanocomposites. Both 2D inorganic hosts exhibit several common properties (e.g., exfoliation/intercalation, hydrophilic character, ion exchange capacity and biocompatibility). However, MXenes are conductive solids unlike clays. The simultaneity of electrical conductivity and hydrophilicity is a very rare feature in inorganic solids endowed with colloidal properties, which can be of great interest for innovative technological applications such as energy storage, sensor devices or bioactive materials for advanced biomedical uses among other applications (3).

Herein, several recent examples of nanoarchitected hybrids based on carbon composites, bioinspired and bionanocomposite materials based on both Clay Minerals and MXenes will be presented and discussed, illustrating their behavior as superabsorbents, antimicrobial hemostatic materials, piezoelectric sensors, among other potential applications (4).

### Acknowledgements

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## Anisotropic photocatalytic micromotors for environmental remediation

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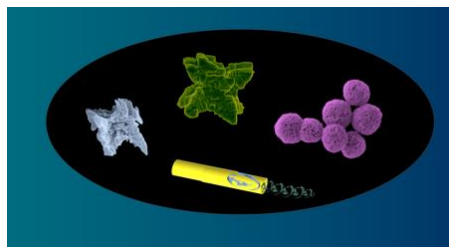
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Photoactivated micromachines are at the forefront of the micro- and nanomotors field, as light is the main power source of many biological systems. Among the different materials that have been explored for the design of light-driven micromotors, photocatalytic-based systems are the most promising due to their fast response to light stimuli, notable speeds, and remarkable chemical stability.<sup>[1]</sup> Here, we present anisotropic  $\text{Ag}_3\text{PO}_4$  and  $\text{BiVO}_4$ -based micromotors, as highly scalable and low-cost micromachines, that can be actuated by turning on/off the light source (Figure 1). The capabilities of these micromotors to interact with the surrounding environment, *e.g.*, metal ions,<sup>[2]</sup> yeast cells, and passive particles were investigated.<sup>[3-4]</sup> Interestingly, we observed that such micromotors adjusted their motion speeds and trajectory in the presence of chemical and biological interferences. Furthermore, we demonstrated that surface molecular imprinting polymer is a promising approach to improve their photoactivity toward the removal of persistent organic pollutants.<sup>[5]</sup> Therefore, photocatalytic micromotors hold promising applications in the fields of photocatalytic disinfection, water treatment, and the food industry.

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### Figures



**Figure 1:** Visible light-responsive photocatalytic micromotors

## Tailoring structural engineering of nanoporous anodic alumina photonic structures by pulse anodization

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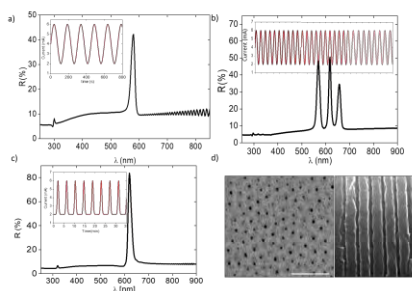
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Photonic Structures (PSs) are one-dimensional photonic crystals with a continuous and periodic variation of their refractive index with depth. They can be obtained based on nanoporous anodic alumina (NAA), formed by the electrochemical anodization of high-purity aluminum by means of an anodization current modulation. The pore modulation of the refractive index results in an interesting optical behavior consisting of a well-defined photonic stop band. Furthermore, several anodization profiles can be overlapped or stacked to produce films with several forbidden photonic bands [1-3]. The optical properties of NAA-RS can be engineered by adjusting several design parameters such as the average anodization current, the current amplitude, the period, and the number of periods of the current component [4-6].

In this work, we report recent results in the structural engineering of one-dimensional NAA photonic structures with different anodization profiles to obtain photonic bands located in the UV-Vis-NIR spectrum range. The effects of fabrication parameters are systematically assessed, revealing that the positions of the characteristic forbidden bands of PCs are highly controllable. Figure 1a shows the reflection spectrum of a photonic structure fabricated with a sinusoidal current profile (inset), and figure 1b shows a reflection spectrum of a photonic structure fabricated with a sinusoidal profile with stack configuration (inset). Figure 1c shows the reflection spectrum of a photonic structure fabricated with a gaussian current profile (inset) and 1d shows the FESEM top view and cross-section respectively of the gaussian photonic structure.

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**Figure 1.** Reflection spectra of (a) Photonic structure with sinusoidal current profile, (b) Photonic structure with sinusoidal current profile in stack configuration, (c) Photonic structure with gaussian current profile and (d) FESEM top view and cross-section of gaussian photonic structure.

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## Spin relaxation in graphene induced by corrugations

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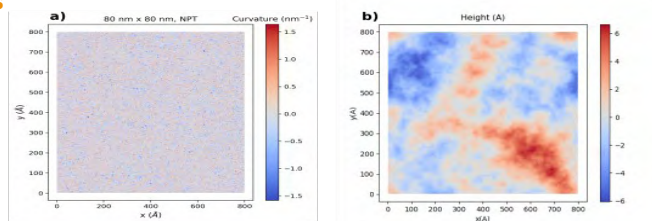
Controlling spin relaxation rate is important to design devices intended to be applied in spintronics. Since spin injection and detection was demonstrated, graphene has been considered to be applied for spintronic devices. One reason is its low spin-orbit coupling, that allows spin to travel further while can be modified via proximity effect with other materials (such as TMDs).

However, studies report spin relaxation times orders of magnitude lower than predicted by theory. In the other hand, atomic disorder in graphene have been predicted by Guinea et al. [2] to possibly have a deep impact in spin orbit interaction. Here we develop a KPM (Kernel Polynomial Method) real space approach [1] combined with Molecular dynamics relaxations to deal with such real space deformation and study them to estimate the contribution of corrugation to the spin dynamics of a corrugated graphene sample in a wide range of gate voltages and make a discussion based on the main spin relaxation processes known.

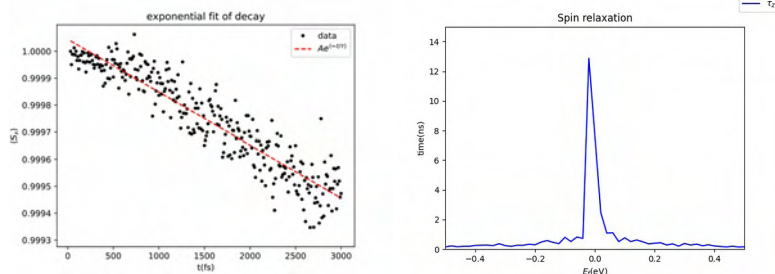
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### Figures



**Figure 1:** Characterization of the MD sample in curvature (left) and height (right)



**Figure 2:** Spin relaxation time depending on the gate voltage at right fitted form spin decay (right)



## Engineering of Charge Current Flow in Nanoporous Graphenes

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During the last decade, on-surface fabricated graphene nanoribbons (GNRs) have gathered enormous attention due to their semiconducting  $\pi$ -conjugated nature and atomically precise structure.<sup>[1]</sup> GNRs are regularly characterized by means of scanning probe microscopy (SPM), which has also allowed to study exotic electronic quantum phases realized in these nanostructured materials.<sup>[2]</sup> A significant breakthrough in the same field was the fabrication of the nanoporous graphene (NPG) as a 2D array of laterally bonded GNRs,<sup>[3]</sup> as sketched in Figure 1. This covalent integration of GNRs could enable complex electronic functionality at the nanoscale, particularly if one could tune the electronic coupling between GNRs within NPGs. In this talk I will summarize recent efforts towards controlling current flow within NPGs either via rational chemical design<sup>[4]</sup> or via external means such as electrostatic gates.<sup>[5]</sup> Our most recent studies, based on quantum chemical calculations and large-scale transport simulations, generalize these ideas to other types of carbon nanostructures<sup>[6]</sup> and, importantly, demonstrate their applicability under practical use conditions, such as including the effect of electrostatic disorder or finite temperature (see Figure 1). A fundamental strategy to design carbon nanodevices with built-in externally tunable electronics is thus proposed, and should be key for future applications such as bio-chemical nanosensing and carbon nanoelectronics.

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### Figures

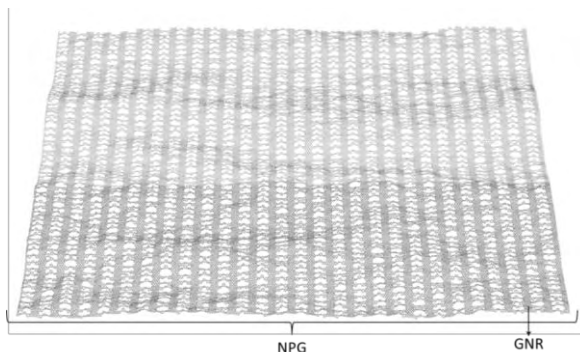


Figure 1: NPGs are made as 2D arrays of laterally connected parallel GNRs.

## Debye length domain for ion migration in metal halide perovskites for X-ray detection

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The research on metal halide perovskites as absorbers for X-ray detection<sup>[1]</sup> is an attractive subject due to the optimal optoelectronic properties of these materials for high-sensitivity applications. However, the contact degradation and the long-term instability of the current limit the performance of the devices, in close causality with the dual electronic-ionic conductivity of these perovskites. Herein, millimeter thick metal halide perovskite (e.g. MAPbI<sub>3</sub>,<sup>[2]</sup> MAPbBr<sub>3</sub>,<sup>[3]</sup> CsPbBr<sub>3</sub>)<sup>[4]</sup> samples are approached by characterizing their long-term dark current upon biasing and afterwards at short circuit. Experimental measurements and numerical MATLAB's Driftfusion simulations are employed. First,<sup>[5]</sup> the mobile ion concentration and mobility are correlated with three main transport regimes and interpretation and parameterization are provided to the current saturation time in terms of the ionic screening of the electric field toward the interfaces upon biasing. The final steady-state under reverse biasing is found as diffusion-limited electronic current, which results from abrupt mobile ion depletion proportional to the Debye length in the vicinity of a contact. The conclusions suggest the material optimization of the contact interfaces as a pathway to reduce the long current saturation times in these devices. Subsequently,<sup>[6]</sup> upon removal of the biasing, it is shown how both the dark current and the sensitivity of the detectors follow similar trends at short-circuit ( $V=0$  V). Large ionic-related built-in fields not only produce relaxations to equilibrium lasting up to tens of hours, but also continue to affect the charge kinetics under homogeneous low photogeneration rates. Furthermore, a method is suggested for estimating the ionic mobility and concentration by analyzing the initial current at short-circuit and the characteristic diffusion times.

### Acknowledgements

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## Brain tumor mutated DNA detection with 2- and 3-terminal graphene devices

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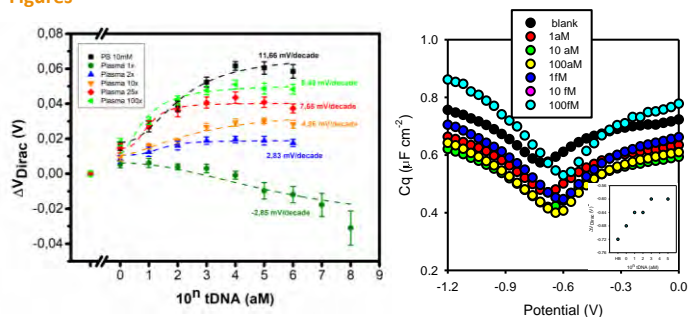
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Brain tumors are detected by expensive and invasive techniques, effective only when the disease is already in advanced stages. Liquid biopsies have recently emerged as a promising method for early cancer detection and represent a minimally invasive way to capture tumor activity in real time. In the case of malignant glioma, particular biomarkers with clinical relevance were identified, e.g., the TERT promoter mutation at position C228T.<sup>1</sup> Mutations are detected by polymerase chain reaction (PCR) and next-generation sequencing (NGS), either for whole genome sequencing or massive sequencing of the target region. The detection process is long, complicated, and costly. Therefore, a high-sensitivity and high-specificity detection method is needed to detect ultra-low concentrations of circulating tumoral DNA early and fast. In this work, a 25-mer sequence containing the C228T mutation (tDNA) is detected using a complementary strand, immobilized on graphene 25  $\mu\text{m}$  x 75  $\mu\text{m}$  channels. The channels – 20 per chip – are contacted with Au source and drain terminals for electrical transducing of the biorecognition events. A large, coplanar Au electrode surrounds the channel region.<sup>2</sup> The 10  $\mu\text{L}$  droplet containing the mutated DNA diluted in a buffer or human plasma is placed over the 20 functionalized graphene channels. The detection is achieved by operating each transducing device as a 3-terminal liquid-gate transistor (GFET) or a 2-terminal electrochemical impedance electrode (GEE). In the latter case, the chip's source and drain output pads are short-circuited, and the planar gate works as the counter-electrode. In transistor mode, the chips detected the tDNA down to the attomolar range ( $\sim 10$  aM) by following the charge neutrality point voltage in the GFET transfer curves. In the GEE mode, the signal was obtained from impedance-derived capacitance spectroscopy by following the minimum of the graphene quantum capacitance as a function of bias potential at a specific low-frequency limit,<sup>3</sup> with a limit-of-detection of 1 aM. These results encourage the pursuit of an integrated, low-cost, ultra-sensitive biosensor to detect circulating tumoral DNA based on single-layer graphene microdevices.

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### Figures



**Figure 1:** a) Calibration curves for GFET detection of tDNA in PB and plasma. b) Graphene quantum capacitance measurements for different tDNA concentrations in human plasma. The inset shows the Dirac point movement as a function of tDNA concentration.

## Contribution to the study of the encapsulation of microorganisms (cyanobacteria and yeasts) in clay and silica based matrices

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### Abstract

Encapsulation of microorganisms in inorganic matrices is being widely studied in recent years [1]. One of the key objectives is to achieve cell protection that facilitates their use in various applications, e.g. for biocatalytic preparation of specific products. Ideally, to protect them, the matrices generated must be biocompatible, resistant and translucent, allowing the maintenance of their metabolic functions while limiting cell division. The advantage of the immobilization of microorganisms as a biocatalytic system lies in its ease of handling, and especially in the simplicity and efficiency of the recovery of the produced compounds. In this communication it is compared the characteristics and performance of biohybrid materials based on silicic matrices prepared via sol-gel and bionanocomposites based on biopolymers and clays (sepiolite), for the encapsulation of cyanobacteria (*Synechococcus elongatus* PCC7942) and yeasts (*Saccharomyces cerevisiae*). On the one hand, it has been evaluated the potential use of matrices based on bionanocomposites of chitosan and alginate that incorporate sepiolite produced as films, beads or foams for the immobilization of cyanobacteria, analyzing the problems that they may present for the long-term survival of the encapsulated microorganisms. On the other hand, it has been analyzed the use of silica-based matrices generated by sol-gel. The use of silica gels to encapsulate bioactive microorganisms, such as algae and cyanobacteria, have demonstrated a good way to obtain biocompatible, resistant and translucent matrices [2]. In the present study the silica gel matrix was generated from sodium silicate and treated to reduce its sodium content in view to directly entrap cyanobacteria and yeasts or once modified to produce "yolk-shell" type systems [3]. The so-called "yolk-shell" structures seek to create a silica cover around the cells in a system similar to that of an egg by protecting the cell with a protein (protamine) around which the silicic capsule is created. In particular, it has been verified how the coating of unicellular microorganisms with a silica shell reduces contact between the cells and the inorganic matrix and increases their durable survival by maintaining bioactivity more efficiently [4]. Thus, for example, encapsulated yeast is capable of producing ethanol for several days, confirming the potential of this approach for applications related to biocatalysis.

### Acknowledgements

Financial support by the MCIN/AEI/10.13039/501100011033 (Spain, project PID2019-105479RB-I00) is acknowledged. Authors also thank 4C Fuels project (iGEM Team MADRID\_UCM 2021) and the CSIC-UAM agreement for the training of undergraduate students.

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## Stability of carbon supported platinum particles (Pt/C): Effect of dispersant and pH

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Carbon supported platinum particles (Pt/C) are used as catalysts in proton exchange membrane fuel cells (PEMFCs). They promote the oxidation of hydrogen on the anode and the reduction of oxygen on the cathode. [1] The catalyst layers for the PEMFCs are produced as ink formulations which are then applied directly on the membrane by means of different solution-coating methods (e.g. ultrasonic spray coating). The formation of a homogeneous coating layer depends on the ink formulation and processing steps. [2]. In order to optimize the viscosity and the surface area, the main goal of the ink processing is to obtain well dispersed Pt/C suspensions. [1]

We investigated the effect of the dispersing solvent and surfactant on the particle size, size distribution as well as on the surface charge (zeta potential) of carbon black and Pt/C particles. The impact of the pH value was also monitored by using a dynamic light scattering system equipped with an automatic titration unit.

The narrow particle size distribution as well as the strongly negative zeta potential measured for Pt/C particles confirm the stabilizing effect that platinum particles have for the carbon support.

However, mixed with a KCl and surfactant solution, the Pt/C particles show a high agglomeration tendency at pH < 5 in comparison with a dispersion of the particles in distilled water and surfactant. In the acidic range the ionic strength of the solution causes a compression of the electric double layer present on the particle surface leading to a decrease of electrostatic repulsion and thus resulting in a lower magnitude of the zeta potential.

Information about particle size and formulation stability are of high importance in the design of experiment phase for the characterization of major properties, which can have an impact not only on the catalyst layer production but also on the fuel cells performance.

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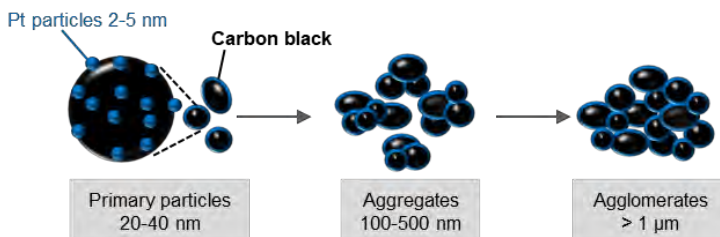


Figure 1: Carbon support of Pt/C catalyst as primary particles, aggregates and agglomerates. Adapted from [2]

## Development of functionalized microchips for intracellular GSH sensing using BODIPY derivatives as fluorescent probes

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### Abstract

Molecular imaging based on fluorescent probes is a technique providing online fluorescence sensing of biomolecules<sup>1</sup>. On the other hand, self-assembly monolayers (SAMs) are considered a key tool in the surface design of nanolayers for the bioactive coating of biomedical devices<sup>2,3</sup>. Our main target is intracellular GSH sensing with micro-sensors providing efficient cellular uptake of fluorescent probes, long-term tracking, and overcoming optical instability and biotoxicity.

Two types of GSH probes based on BODIPY derivatives were synthesized and conjugated to the surface of silicon oxide microchips. Functionalized microchips were finally released in suspension from the wafer by using a mounting medium and characterized by confocal microscopy. The sensitivity of Functionalized microchips was studied in the GSH solution. The cell internalization of functionalized microchips and their sensitivity to the intracellular GSH were also investigated in HeLa cells.

Project PID2020-115663GB-C3 was funded by MCIN/AEI/10.13039/501100011033. We also thank AGAUR (Generalitat de Catalunya) for a grant to consolidated research groups 2021 SGR 01085. S. B. thanks Generalitat de Catalunya for a predoctoral FISDUR scholarship.

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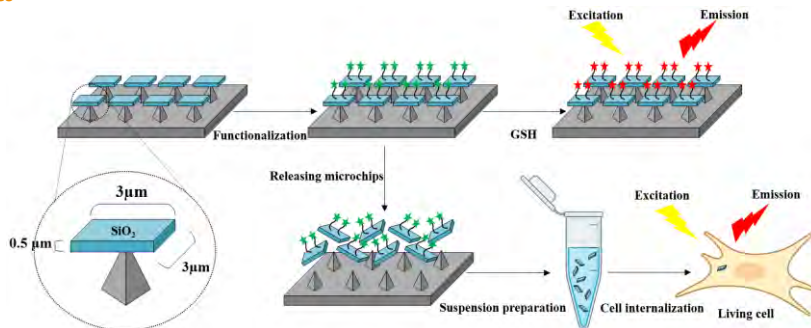


Figure 1: Schematic of surface functionalization of silicon oxide microchips and GSH sensing experiments

## Eco-friendly synthesis of a porous graphene-like material supported on clay

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The graphene derivatives are nanomaterials of great interest due to their distinctive physicochemical properties and versatile application in a wide range of fields. However, a challenging large-scale synthesis compromises their commercialization.<sup>[1]</sup> The development of eco-friendly strategies using non-toxic precursors, energy- and time- saving methods is necessary to reduce costs, mitigate the environmental impact, and facilitate the industrial production.<sup>[2]</sup> In this regard, the synthesis of carbon nanomaterials using natural precursors, such as clays and table sugar, is a step forward to address this issue.<sup>[3]</sup>

In this work, sucrose and sepiolite clay were used to prepare supported graphene-like materials at low temperatures. Moreover, we investigated the effect of the synthesis conditions: i) temperature of 200/500 °C; ii) type of furnace - tube furnace or a microwave muffle; and iii) post hydrothermal carbonization (HTC) step, on the carbon nanomaterials obtained. The structure, morphology and porosity of the carbon nanomaterials were characterized by STEM, ATR-FTIR, Raman spectroscopy, XRD, HRTEM, and N<sub>2</sub> adsorption-desorption isotherms. The morphology analysis revealed sepiolite fibres well blended with carbon. The structural analysis indicated that sucrose melted at 200 °C blocking the sepiolite pores. However, the post HTC provided a fundamental contribution to enhance the carbonization and develop the porosity ( $S_{\text{BET}}$ : 76-158 m<sup>2</sup>g<sup>-1</sup>). The materials produced at 500 °C presented higher specific surface areas ( $S_{\text{BET}}$ : 264-275 m<sup>2</sup>g<sup>-1</sup>) without requiring the post HTC step. In both cases, the materials synthesised using the tube furnace presented higher specific surface area than the ones synthesized using the microwave muffle. The HRTEM investigations showed that the carbon nanomaterials synthesized using the microwave were mainly amorphous, while the ones synthesized in the tube furnace were dominated by crystalline areas. The crystalline sample synthesized at 500 °C presented a d-spacing of 0.33 nm, which coincides with the graphitic lattice suggesting the formation of well-organized multilayer graphene, which is remarkable for occurring at temperatures as low as those adopted here. The supported graphene-like material, obtained with methodologies compatible with the large scale-production, displays suitable properties for the development of functional composite materials.

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## ELECTROCHEMICAL DETECTION OF REDUCED GRAPHENE OXIDE IN WATER

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### Abstract

Many products used in everyday life are made with the assistance of nanotechnologies. Industry, agriculture, medicine and electronics are only a few examples of fields that extensively used nano-sized particles (NPs), generally added to improve product quality [1]. Of these, carbon-based nanoparticles (CNPs) represent one of the most promising products in the field of nanotechnology. For example, graphene oxide (GO) and its derivatives have attracted much attention in industrial applications due to its fascinating properties such as high dispersion in aqueous media, hydrophilicity, surface functionalization ability and high biocompatibility [2]. Because of the wide spectrum of usage of these materials, toxicity to the environment and living organisms has been reported, raising concerns about their utilization [3]. For these critical reasons, the development of analytical methods for the detection of CNPs at trace concentrations has become a very important subject of research. Until now, only a few studies were reported on the detection of CNPs. Almost all of them used nano-impact electrochemistry method [4–6]. This method can provide information about size distribution, mass-transfer, and concentration of single NPs. But the selectivity toward the NPs and the effects of environmental interferences are not understood yet. Voltammetry methods can be a good answer for selectively detecting and quantifying of CNPs in water samples. Voltammetric detection is performed by measuring the generated redox current of the targeted NPs related to the particles concentration. This strategy has been recently used for the detection of silver nanoparticles [7] and carbon nanotube [8].

In this work, carbon screen printed electrodes were employed for the investigation of electrochemical response of reduced GO (rGO) through differential pulse voltammetry (DPV) method. First, rGO was characterized by temperature-programmed desorption method, scanning electron microscope (SEM), dynamic light scattering, and Raman spectroscopy. The influence of rGO dispersing solution concentration on the sensor response was also tested. Next, DPV, electrochemical impedance and SEM characterization of the sensor before and after detection were carried out. Under the best experimental conditions, the sensor exhibited good performance in terms of linear range (from 1 to 50 µg/mL) and detection limit of 2.5 µg/mL. Finally, the reproducibility, selectivity and practical application in water samples were examined.

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## Bioinspired Antibacterial Catechol-Amine Coatings

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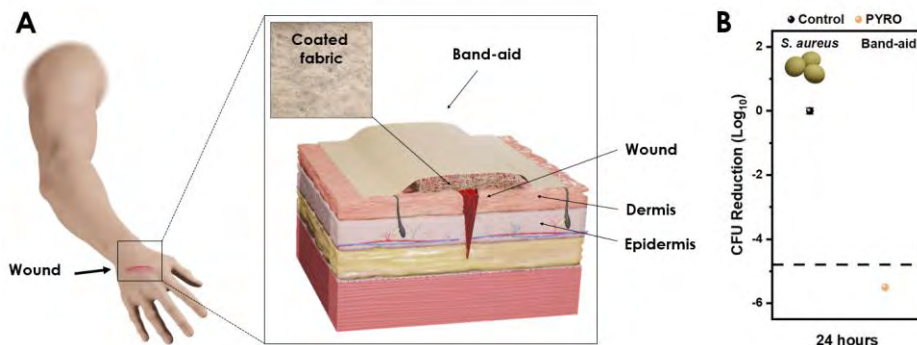
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The use of **catechols** as functionalizing agents or ligand in the formation of bioinspired materials has been increasing during the past years due the outstanding properties offered by these molecules [1]. Besides, the constant search of new **antimicrobial surfaces** and **fabrics** has increased the use of antibiotics and metallic nanoparticles, among others. However, the functionalization of coatings with them usually implies drawbacks like the leaching (with its consequent loss of activity), as well as the possibility of being toxic for humans.

In this study, combinations of catechol-derivatives (specially **Pyrocatechol** and **Caffeic acid**), with Hexamethylenediamine ligands were performed to obtain coatings on broadly used fabrics (cellulose, cotton and polypropylene) and band-aids, creating and homogeneous and hydrophilic thin-layer over them. The **antibacterial properties** of these materials were determined by counting the colony forming units (CFU) decrease of several pathogenic bacteria, mostly found in hospital environments, achieving reductions near to an outstanding **99,999%**. Worth to mention, the catechol-based coatings are obtained through an **affordable, straightforward** and **environmentally-friendly** production, avoiding the use of harmful solvents, metals or antibiotics and being **compatible** with a broad range of materials. Therefore, this universal and bioinspired platform could be an excellent choice to tune the properties of different fabrics and increase the range of their applications.

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**Figure 1:** Catechol-amine coated Band-aids. a) Schematic proposed application in wound healing. b) CFU reduction obtained with *Staphylococcus aureus*.

## Standardizing Porous Silicon to Enable Cutting Edge Research and High-Tech Industrial Applications.

Chris Burns, Alex Pöchheim

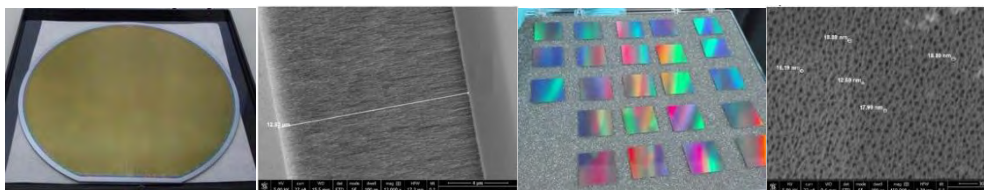
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Although accidentally discovered by testing the extremes of standard semiconductor processes, Porous Silicon has become a material that has exploded into so many different fields such as the medical, energy, semiconductor, and material enhancement just to name a few. Due to its relative ease of morphology tuning to enhance specific material properties and property windows, it is playing a big role in the background of many new breakthroughs. Properties such as high and specific surface area, pore volume, optical or refractive index, color etc. In combination with silicon's capabilities to not only be biocompatible, but also biodegradable, the door for insitu medical applications is also now wide open. One of the difficulties, however, of porous silicon is its flexibility. It can be used practically everywhere, and each optimized application requires slightly different material characteristics, therefore standards and industrialization has proven to be slightly difficult. At The Porous Silicon Company, a few standards have been categorized in the microporous, mesoporous, and macroporous ranges. This presentation aims at categorizing these three separate morphology ranges into common applications for each range. This should act as a roadmap to help and give researchers or industrial engineers looking to incorporate the material and give an indication of where to start and which materials to try first in order improve their current applications and give new impulses for applicatons to come.

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### Figures



**Figure 1:** An assortment of microporous, mesoporous and macroporous silicon with SEM pictures of the morphologies as well as pictures showing its optical versatility.

## Antimicrobial peptide-grafted PLGA-PEG Nanoparticles to Fight Bacterial Wound Infections

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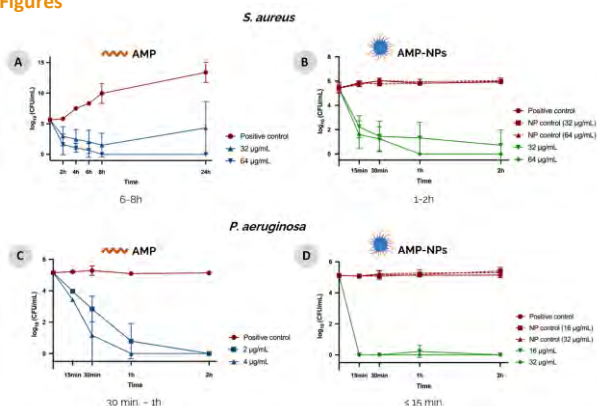
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The treatment of chronic wound infections (CWI) using antimicrobial peptides (AMPs) is not yet effective as they lose their activity *in vivo*. In this work, the AMP MSI-78(4-20) was grafted to poly(D,L-lactide-co-glycolide)-polyethylene glycol (PLGA-PEG) nanoparticles (NPs) through a thiol-maleimide (Mal) Michael addition reaction. As opposed to encapsulation, this strategy prevents AMP aggregation and accelerates AMP action. MSI-78(4-20) is a shorter derivative of MSI-78, that shows equivalent antimicrobial action and further selectivity towards bacterial cells [1]. Different ratios of PLGA-PEG/PLGA-PEG-Maleimide (Mal) were tested, and the formulation containing 40% PLGA-PEG-Mal displayed the best colloidal properties and the highest AMP content, as evidenced by NPs zeta potential ( $+8.6 \pm 1.8 \text{ mV}$ ) and AMP quantification ( $326 \mu\text{g/mL}$ ). Regarding the antimicrobial performance, AMP-NPs proved to be as effective as the free AMP with a minimal inhibitory concentration (MIC) of  $8\text{--}16 \mu\text{g/mL}$  against *Pseudomonas aeruginosa* and  $32\text{--}64 \mu\text{g/mL}$  against *Staphylococcus aureus*. In addition, AMP grafting reduced the time for complete killing from 1-2h to 15min for *P. aeruginosa* and from 6-8h to 0.5-1h for *S. aureus* (Figure 1). When tested in simulated wound fluid, AMP-grafted NPs maintained the antimicrobial activity against *S. aureus* while loss of activity was observed against *P. aeruginosa*. Importantly, at the MIC concentrations ( $16$  and  $32 \mu\text{g/mL}$ ) AMP-NPs did not cause cytotoxic effects on human foreskin fibroblasts with respect to their metabolic activity. To sum up, our findings support that AMP-PLGA-PEG NPs represent a promising approach to manage CWI.

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### Figures



**Figure 1:** Time-kill assay of AMP (A) and AMP-NPs against *S. aureus* (B); and AMP (C) and AMP-NPs against *P. aeruginosa* (D).

## Comparison of xylose-derived and glucose-derived carbon quantum dots (CQDs) prepared by microwave-assisted synthesis

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The development of technologies to produce energy and chemical products from renewable resources has promoted the valorisation of biomass. Lignocellulose is the most abundant and least expensive of renewable biomass, containing cellulose (40-50%), hemicellulose (25-35%) and lignin (15-20%) [1].

One challenging way of revalorising lignocellulosic biomass is by synthesising CQDs, which are nanomaterials with sizes below 10 nm and attractive properties, such as facile synthesis, high hydrophilicity, chemical stability, and unique luminescent properties [2]. CQDs may have a graphite core and an amorphous shell with carboxyl, hydroxyl, amide, and carbonyl moieties, giving them tuneable photoluminescence (PL) and even up-conversion properties under excitation above 800 nm [3]. CQDs may exhibit strong absorptions in the UV range and visible photoluminescence, with quantum yield exceeding 80% [4].

This work aims to synthesise and characterise CQDs from the lignocellulosic biomass fractions xylose and glucose, obtained by almond shells (Cooperativa Unió Nuts, Reus), using microwaves for a more energy-efficient, faster and greener process than traditional synthesis methods. The unpurified samples were characterized by UV-vis absorption, Zetasizer, Transmission Electron Microscopy (TEM), emission and excitation spectrometry, and the results compared. Special emphasis was put in the optimization of the synthesis conditions, rarely discussed in the literature.

Xylose-derived CQDs were 2-5 nm in size, whereas glucose-derived CQDs were 2-10 nm in size. Slight differences in the PL properties were observed when using xylose or glucose as carbon precursors. Additionally, their PL properties were different depending on the pH used.

These results have been possible through grant PID2021-128090OB-C22, TED2021-129487B-C31 and EIN2020-112210 funded by MCIN/AEI/10.13039/501100011033 and "ERDF A way of making Europe" and "European Union NextGenerationEU/PRTR". We also thank Generalitat de Catalunya by funding through projects 2021 SGR 00658 and 2021 FI SDUR 00181.

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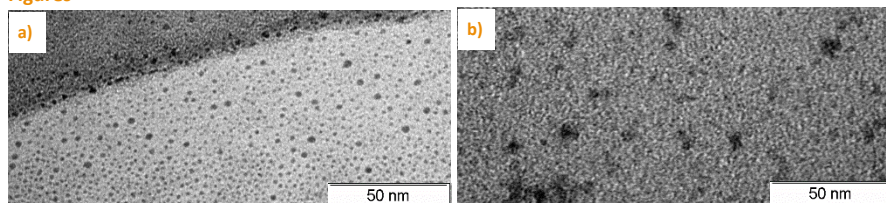


Figure 1: TEM Image of a) xylose-derived CQDs and b) glucose-derived CQDs.

## Thermosensitive Magneto-Fluorescent Nanoplatforms with Great Heating Power

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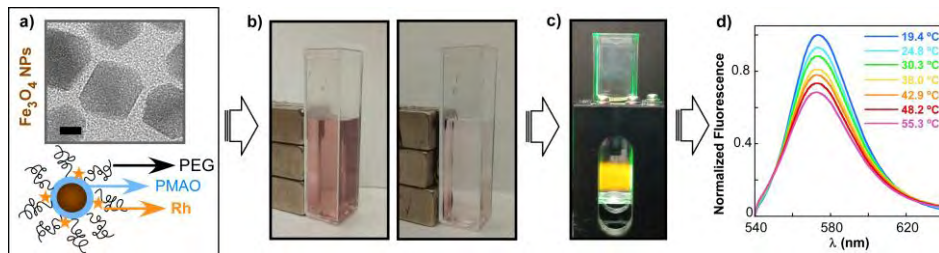
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Nanosystems that simultaneously contain magnetic and fluorescent modules can offer decisive advantages in the development of new biomedical technologies. Magnetite NPs-based structures have shown a lot of potential in magnetically-driven diagnostic and therapeutic modalities, such as magnetic resonance imaging (MRI) and magnetic hyperthermia (MH), respectively<sup>1</sup>. On the other hand, Rhodamine 3B is a biocompatible fluorophore whose emissive properties are pH independent (above 6) and insensitive to the ionic strength, but presents fluorescence quantum yield that linearly decreases with temperature<sup>2</sup>. There is not doubt that a nanomaterial that includes efficient nanoheaters together with luminescence and an intrinsic temperature sensor would become a promising theranostic agent. In this work, we have developed a magneto-fluorescent nanoplatform that incorporates Fe<sub>3</sub>O<sub>4</sub> NPs with large magnetothermal actuation and thermosensitive rhodamine (Rh) molecules that have the ability to self-monitor the hyperthermia degree (Figure 1). The size (~25 nm) and shape (octahedral-like) of the magnetite NPs have been finely tuned (Figure 1a) in order to reach an optimal heating capacity within the clinical safety limits (~1000 W/g at 142 kHz and 44 mT). Several copolymers formed by poly(maleic anhydride-alt-1-octadecene) (PMAO), polyethylene glycol (PEG) of high molecular weight and Rh have been prepared to coat the magnetite cores and avoid strong dipolar interactions among NPs. The optical study has revealed that copolymers synthesized with PEG of 20 kDa and a 10 % rhodamine fulfill the best compromise to achieve Fe<sub>3</sub>O<sub>4</sub>@Rh nanoplatforms with good fluorescent efficiency, minimal aggregation and suitable thermosensitivity (0.9 % °C<sup>-1</sup>) (Figure 1d).

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### Figures



**Figure 1.** a) TEM image (scale bar 10 nm) and a drawing of the Fe<sub>3</sub>O<sub>4</sub>@Rh nanoplatforms, b) Fe<sub>3</sub>O<sub>4</sub>@Rh colloid close to a magnet (initially and after 24 h), c) fluorescence emission of a Fe<sub>3</sub>O<sub>4</sub>@Rh sample and d) the evolution of the fluorescence at different temperatures.



## Hybrid nanostructured compounds of Mo<sub>2</sub>C on vertical graphene nanoflakes for highly efficient hydrogen evolution reaction.

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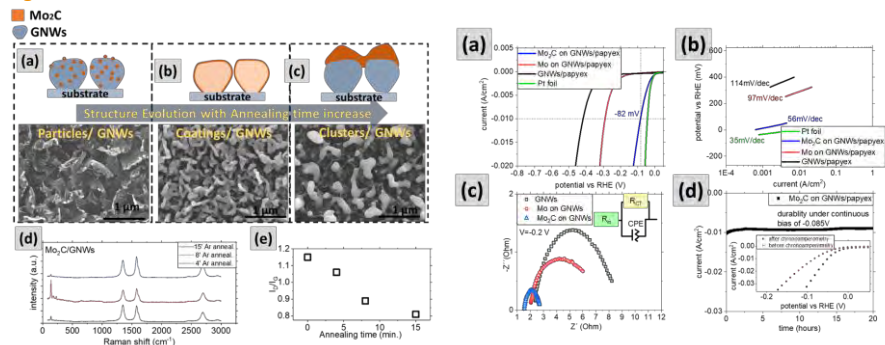
### Abstract

Organizing a post fossil fuel economy will require the prior development of sustainable energy carriers. Hydrogen is expected to play a significant role in this direction, being the most efficient one, thus nowadays it exists an emerging demand regarding its production. Green hydrogen produced by water splitting produces zero carbon emissions but requires the use of expensive catalysts. Therefore, the demand for efficient and economical catalysts is constantly growing. Transition metal carbides, and especially Mo<sub>2</sub>C, have attracted a lot of attention since they are earth-abundant and hold great promises for efficient performance towards the hydrogen evolution reaction [1]. The present study presents a bottom-up approach for the deposition of Mo carbides nanostructures on vertical graphene nanowalls templates [2], combining chemical vapour deposition, magnetron sputtering and thermal annealing processes. Results highlight the importance of adequate loading of graphene templates with the optimum amount of Mo carbides, controlled by both deposition and annealing time (Fig. 1), to enrich the available active sites. The resulting compounds present exceptional activities towards HER in acidic media, requiring overpotentials of 82 mV at -10 mA/cm<sup>2</sup>, and demonstrating a Tafel slope of 56 mV/dec (Fig. 2). The high double-layer capacitance and low charge transfer resistance are spotlighted as the main causes of the enhanced HER activity. These results are expected to pave the path toward the design of novel hybrid nanostructures based on nanocatalysts deposition on three-dimensional graphene templates.

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### Figures





## Time-resolved MOKE and GMI effects in Co-rich Amorphous Ribbons

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Recent development of the ultrafast spectroscopy provides a unique tool to access elementary scattering and relaxation processes by optically exciting the electronic and spin subsystems [1]. A particular interest is amorphous microwires and ribbons exhibiting giant magnetoimpedance (GMI) effect. We present the study of magnetization precession in a Co-rich ribbon induced by femto-second laser pulses. We deduce the frequency and amplitude of the magnetization precession as a function of the laser intensity (Fig. 1).

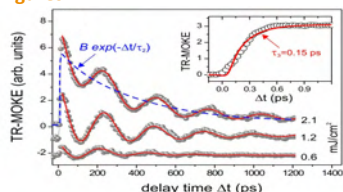
The magnetization precession is triggered by a thermal change in the effective field of the magnetic anisotropy on a single-picosecond timescale. We reveal a correlation between the frequency of magnetization precession obtained by laser induced excitation and the resonance frequency of GMI response. These results enable detection of the GMI effect in the ultrahigh-frequency regime, which appears highly attractive for gigahertz applications.

The improvements in the properties of GMI materials will facilitate the development of multifunctional composites suitable for wireless and nondestructive monitoring of external stimuli [2]. Thermal processing of metallic ribbons provides a fruitful playground for engineering their properties. During annealing at low temperatures, changes in the internal stress in amorphous metallic ribbons result in an improvement of their magnetic softness and modification of the surface magnetic anisotropy. The GMI effect in these ribbons is sensitive to annealing. Local ultrafast heating of such ribbons by femtosecond laser pulses may have an impact on their transient GMI response. Substituting annealing procedures with laser heating may open up additional possibilities for tuning the properties of the ribbons.

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### Figures



**Figure 1:** Time-resolved Kerr rotation as a function of the delay time  $\Delta t$  for several fluences of the pump. The inset shows the time-resolved Kerr rotation for pump fluence of 2.1 mJ/cm<sup>2</sup>.

## Hot-spots in Plasmonic Photocatalysis

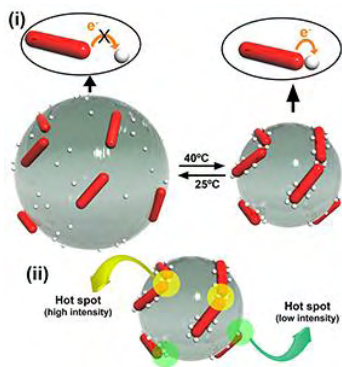
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### Abstract

Herein, we introduce a novel approach for achieving a real-time control over the hot-electron injection process in metal-semiconductor photocatalysts. Such functionality is attained through the design of a hybrid nanocomposite in which plasmonic Au nanorods and TiO<sub>2</sub> nanoparticles are synergistically integrated with a thermoresponsive polymer. In this manner, modifying the temperature of the system allows for (i) the precise regulation of the interparticle distance between the catalyst and the plasmonic component, and (ii) the reversible formation of plasmonic hot spots on the semiconductor. Both features can be simultaneously exploited to modulate the injection of hot electrons, thus boosting/inhibiting at will the photocatalytic activity of these heterostructures. This innovative conception enables a dynamically adjustable performance of semiconductors, hence opening the door to the development of a new generation of plasmon-operated photocatalytic devices.

### Figures



**Figure 1:** Representation of the collapse-swelling transition experienced by the Au-TiO<sub>2</sub>/pNIPAM nanohybrids leading to, (i) the control of the electron injection on TiO<sub>2</sub> by tuning the interparticle distance between the semiconductor and the plasmonic material, and (ii) the reversible formation of interparticle hot spots.

## Dhvar5-Chitosan Nanogels Generated by Microfluidic Fighting Orthopedic Device-Related Infections

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Orthopedic Device-Related Infections (ODRIs) are a major medical challenge, due to the involvement of biofilm-encased and multidrug-resistant bacteria, and due to the inefficiency of current therapies based on antibiotic administration [1-2]. Therefore, there is the need for antibiotic-free alternatives [3]. Antimicrobial peptides (AMPs) are a promising solution due to their broad-spectrum of activity, high efficacy at very low concentrations, and low propensity to induce resistance [4]. We aim to develop a new AMP-based chitosan nanogel coating to prevent ODRIs. Chitosan was functionalized with norbornenes (NorChit) through the reaction with carbic anhydride [5] and then, a cysteine-modified AMP Dhvar5 was covalently conjugated to NorChit (NorChit-Dhvar5), through a thiol-norbornene photoclick chemistry, under UV-photoactivation [5]. Characterization was done by Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance spectroscopy (NMR) analyses, and a successful functionalization of chitosan with norbornenes and posterior Dhvar5 immobilization was proved. For NorChit-Dhvar5 nanogels production, the NorChit-Dhvar5 solution (0.15% w/v) and Milli-Q water were injected separately into a microfluidic system. The nanogels were characterized regarding size, concentration, shape, and charge, using Transmission Electron Microscopy (TEM), Nanoparticle Tracking Analysis (NTA) and Dynamic light scattering (DLS). The nanogels antibacterial properties were assessed in Phosphate Buffer (PBS) for 6 h, against four relevant microorganisms (*Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *S. aureus* methicillin-resistant (MRSA)), and in Muller-Hinton Broth (MHB), 50% (v/v) in PBS, supplemented with human plasma (1% (v/v)), for 6 and 24 h against MRSA. The obtained NorChit-Dhvar5 nanogels, presented a round-shaped, ~100 nm and positive charge. NorChit-Dhvar5 nanogels in a concentration of 10<sup>10</sup> nanogels/mL in PBS were capable of reducing the initial inoculum of *E. coli* by 90%, *P. aeruginosa* by 99%, *S. aureus* by 99%, and *S. aureus* MRSA by 90%. These results were corroborated by a 99% *S. aureus* MRSA reduction, after 24 h in medium. Furthermore, NorChit-Dhvar5 nanogels do not demonstrate signs of cytotoxicity against osteoblastic MC3T3-E1 cells (a pre-osteoblast cell line) after 24 h, having high potential to prevent antibiotic-resistant infection in the context of ODRIs.

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## Miniaturized, label-free Surface Nanosensing, based on Low-Q-Whispering Gallery Modes

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### Abstract

The increasing integration and miniaturisation of analytical processes requires new sensory methods. Especially interactions on surfaces, such as adsorption or desorption of (bio-)molecules or nanoparticles, which occur in native form, i.e. do not have an extra label, are increasingly in demand.

For this purpose, some label-free methods have been developed in the last decades that detect surface processes either electromechanically (Quartz Crystal Microbalance) or optically, such as Surface Plasmon Resonance (SPR), Bio-Layer Interferometry (BLI) or Ellipsometry. In these systems, the optical waves are influenced once per adsorbed molecule, so that many molecules are necessary to achieve sufficient sensitivity. All methods require direct coupling with the transducer and have planar sensor surfaces of relatively large areas in common, which, are difficult to miniaturise. Hence they are not suitable for measurements in microfluidics or three-dimensional systems such as cell arrays.

### Whispering Gallery Modes (WGM)

WGM are light waves that circulate up to  $10^5$  times (Q-factor) by total reflection at the inner surface of a sphere and are therefore influenced many times by an adsorbed molecule. Depending on the difference in refractive index between the sphere and the outer medium as well as the diameter of the sphere, only discrete wavelengths can circulate, all others are cancelled out.

In order to introduce light waves into an optically denser medium, usually light guides are brought tangentially to circular resonators with 30-300 nm diameter, for which Q-factors of  $10^5$  are achieved. For miniaturisation, we used a simpler setup (Fig.1) in which fluorescent dyes are excited inside microparticles. Their emission forms WGMs in the particles. The ad- or desorption of molecules changes both refractive index and particle diameter, resulting in shifts of the WGM resonance frequencies (Fig. 2). With 7-10  $\mu\text{m}$  sized sensor particles and Q-factors of  $10^4$  (low-Q-WGM), we could achieve sensitivities as with SPR or BLI. We present the developed measuring device as well as advantages of the new technology in terms of miniaturisation and microfluidics, which is illustrated by application examples by coating and release kinetics of drugs from nanometre-thin layer-by-layer films (Fig. 3) as well as from protein binding kinetics<sup>[1]</sup>

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### Figures

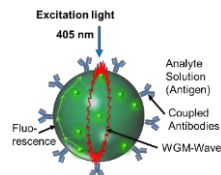


Fig. 1: WGM Sensor Principle

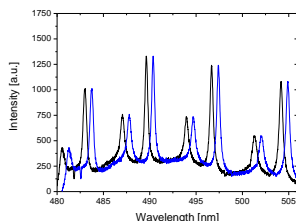


Fig. 2: Emission before (black) and after adsorption of molecules (blue)

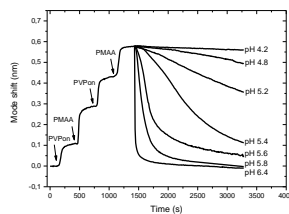


Fig. 3: stepwise adsorption of nanometre multilayers and dissolution

## CNT-based Hybrid Materials as Nerve Guidance Conduits for Sciatic Nerve Regeneration

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The sciatic nerve is the longest and widest nerve fiber in the human body, responsible for supplying sensory and motor functions to the lower part of the body. Any injury to the nerve section or subsequently to the spinal cord can result in loss of the nerve functions <sup>(1)</sup>. Additionally, the formation of neuromas at the lesion site prevents regeneration of the nerve with current treatment being insufficient to regain proper former function <sup>(2)</sup>. Besides nerve transplant and grafting which pose great complications both to the host and the donor, nerve guidance conduits (NGCs) offer a good alternative for nerve regeneration. Current grafts, based on collagen, poly (lactic-co-glycolic acid) (PLGA) and self-assembling peptide amphiphiles (PA) fall short on mimicking the nerve properties <sup>(3)</sup>.

Herein, we present CNT (Carbon Nanotubes) based scaffolds culminating in patentable biomaterials as conduits for nerve tissue regeneration. The hydrogels were synthesized and characterized to study the morphological, chemical, mechanical and electrical properties including rheology analysis, thermal gravimetric analysis (TGA), and sheet resistance. They exhibit a network of interconnected fibres engulfing MWCNT with pore size distribution >10 µm allowing cell penetration. Scaffolds were then optimized for *in-vitro* studies with SH-SY5Y cells showing no cytotoxicity compared to 2D control and possibly favouring growth on CNT scaffolds. Finally, *in-vivo* studies on mouse models with sciatic nerve damage/injury (crush injury and total excision injury) showed better wound healing with CNT scaffolds compared to the control. All mice presented minimal signs of distress and all scaffolds were found to be biocompatible and non-toxic. CNT implants after 3 weeks showed positive nerve regeneration signs.

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### Figures



Figure 1: Schematic representation of nerve guidance conduits based on CNT

## Functionalized nanoparticles for cancer theranostics

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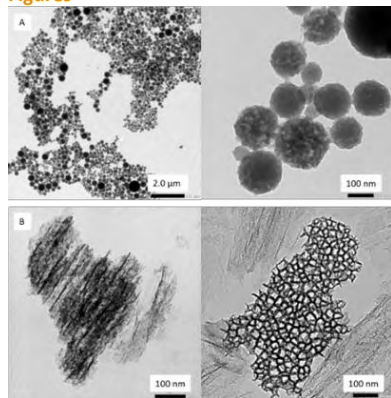
According to the World Health Organization, cancer is the second leading cause of death worldwide[1]. Over the last decade, novel therapeutic approaches sought to offer specially adapted and personalized therapies and alternatives when classic treatments are not enough. Nanomedicine is a sub-field of medicine that focuses on applying nanotechnology and nano-sized tools helping to reduce short and long-term side effects and increase therapeutic efficacy.

Herein we described two complementary nanomaterials, namely porphyrin-based mesoporous organosilica nanoparticles (PMOsPOR-NPs) and porous silicon nanoparticles (pSiNP), which offer benefits over other nanoparticles for a wide range of applications due to their outstanding properties, including large specific surface area[2], tunable pore diameter[2], high loading capacity[3], their biocompatibility and biodegradability[4,5]. Their tailor-made preparation and functionalisation with target molecules to efficiently perform two-photon excitation photodynamic therapy (TPE-PDT)[6] or gene delivery will be presented.

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### Figures



**Figure 1:** TEM images of the nanomaterials (A) PMOsPOR-NPs at different magnifications (B) Different views of pSiNPs.

## Development and Mechanistic Study of $\text{Mn}(\text{CO})_3$ Single Sites in 2D-Covalent Organic Frameworks for Electrocatalytic $\text{CO}_2$ Reduction

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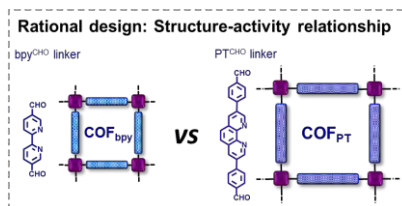
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Global warming, climate change and our over-dependence on non renewable fossil fuels demand long-term solutions to reduce  $\text{CO}_2$  emissions and develop sustainable energy technologies. The electrochemical  $\text{CO}_2$  reduction has the potential to accomplish a “carbon-neutral energy cycle”, which incorporates  $\text{CO}_2$  as the unlimited carbon source for the production of high-density fuels. In this regard, this work entails a fundamental understanding of the  $\text{CO}_2$  mechanisms using Mn Single Atom Catalyst (SAC) within Covalent Organic Frameworks (COFs). The catalytic activity of the materials was benchmarked against other molecular supported catalysts reported in the literature. Compared to equivalent Mn derivatives, COFs exhibited higher selectivity and activity towards  $\text{CO}_2$  reduction. Additionally, mechanistic studies based on *in situ* / *in operando* spectroelectrochemical techniques together with DFT calculations were used to detect key catalytic intermediates and correlate the catalytic activity with the mechanical constraints impose to the  $\{\text{Mn}(\text{CO})_3\}$  active sites by reticular framework. Of particular note is the detection of a radical intermediate within a Mn based COFs avoiding the detrimental formation of a dimeric specie determined as a resting state in the catalytic cycle. In addition, a variation of the bipyridyl linker within the COF, by introducing larger phenanthroline ligand, tuned the structural and electronic properties of the catalyst, consequently influencing on the catalytic  $\text{CO}_2$  reduction activity. The presence of both pyridyl and phenanthroline within the COFs was found to increase the activity respect the equivalent molecular catalysts. However, structural parameters like the crystallinity and porosity of the reticular frameworks proved to play an important role in the stability of the catalysts. Overall,  $\{\text{Mn}(\text{CO})_3\}$ -COFs exhibited higher catalytic activity than the equivalent molecular complexes; thereby suggesting the directions for developing COFs as ligands for  $\text{CO}_2$  reduction.

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### Figures





## Viscous electron flow in graphene: Why does the geometry change the electrical properties?

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Electron-electron collisions rules transport properties of graphene over a vast range of temperatures and scales, resulting in novel and unexpected phenomena known as hydrodynamic regime [1]. The hydrodynamic regime is described by partial differential equations [2], which, unlike the Navier-Stokes for conventional fluids, account for electronic inelastic collisions and the effect of magnetic fields. Here, we introduce a finite element-based numerical approach that enables us to solve these equations in arbitrary geometries.

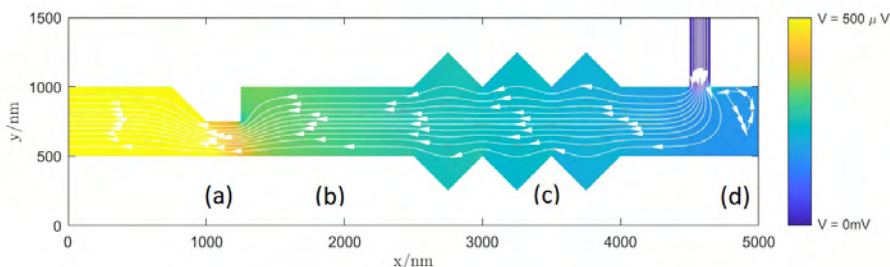
We compute the resistance in a graphene channel and find a strong dependence with the dissipation at the edges, which is modeled by a characteristic slip length. The narrower the channel, the higher this dissipation. We prove two counterintuitive effects: the Gurzhi effect and the fact that the resistance is higher for a wider crenellated channel [3], due to the lack of uniformity in the velocity field. Further reducing the symmetry may result in electronic whirlpools [4]. Last, we study the effect of the magnetic field and the magnetic viscosity, which causes Hall effect and eases conductivity.

We conclude that the geometry has a huge effect on the electrical properties since electron-electron collisions only reveal themselves for non-uniform current fields. Either when modeling graphene devices or when looking for emerging phenomena in unusual geometries, our simulations are an essential tool for a complete understanding of electron viscous flow.

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### Figures



**Figure 1:** Schematic view of a graphene sample at 150 K, with a carrier density of  $10^{12}$  electrons/cm<sup>2</sup>, under a perpendicular magnetic field of 100mT. Electrons, carrying a total current of 100 nA, are injected into the sample by an upper contact, and they leave the sample through another contact on the left. The color scale shows local potentials, which can be used to compute any local or non-local resistance. White lines are streamlines for electron flow. From left to right, we can see (a) a non-symmetrical constriction 250 nm-wide, where there is a large voltage drop due to the reduced width (b) a uniform channel where we can see a Poiseuille flow, together with a Hall voltage, which would increase with increasing magnetic field (c) a crenellated channel where, counterintuitively, the lack of uniformity in the flow results in a larger resistance than in the uniform channel (d) a region of reduced symmetry which leads to an electron whirlpool, where some electrons flow back resulting in negative local resistances, another signature of the viscous electron flow.

## Flexible piezoelectric materials developed using a porous 3D graphite-BaTiO<sub>3</sub> filler

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Piezoelectric composites combine mechanical flexibility and strong electromechanical coupling constants; however, the low dielectric constant of the polymer and the non-continuity of the ceramic may hinder polarization. The low connection between the piezoelectric particles may be addressed using conductive carbon nanoparticles, but the low connection between the piezoelectric phase is left unanswered. Innovative, highly porous 3D carbon networks may overcome these issues. In this work, it is presented an entirely original paradigm in the design and scalable fabrication of high-performance piezoelectric flexible materials enabled by a hierarchic porous graphite network. A 3D graphite network was filled with barium titanate and impregnated with a flexible polymer through two distinct bottom-up methods: hydrothermal and sol-gel syntheses. With the hydrothermal method, the influence of various reaction times on the tetragonality of the particles was studied to perfect a hydrothermal (conventional and microwave-assisted) barium titanate synthesis. With the sol-gel method, the sol is infiltrated on the carbon structure, and a heat treatment capable of forming tetragonal barium titanate while not degrading the carbon template is attempted. The structural phase was assessed using X-ray diffraction and Raman spectroscopy, while the morphology was assessed using SEM. The hydrothermally synthesized particles were used in an optimized water suspension with and without voltage to impregnate barium titanate particles into the graphite foam. Polymeric-based prototypes including the BaTiO<sub>3</sub>-graphite filler were constructed with built-in electrodes, to test the device's electrical output. The structure : piezoelectric output relationship was exploited in both approaches.

**Acknowledgements:** This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). Projects NANOTRONICS (IF/00300/2015); PIEZOFLEX (UTA-EXPL/NPN/0015/2019), FLEXIDEVICE (PTDC/CTM-CTM/29671/2017) are also acknowledged. NETPORE COST CA 20126 (European Cooperation in Science and Technology) is thanked for the support .

## An universal one-pot microfluidic system to produce nanoparticles decorated with antimicrobial compounds

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Antibiotic resistance is a main public health challenge, being described by the World Health Organization as “one of the biggest threats to global health & development today”. The use of antimicrobial peptides (AMPs) is gaining relevance as an alternative to antibiotics. PexigananA (MSI-78A) is an analog of Pexiganan with reported bactericidal activity against *Helicobacter pylori* (Hp), a gastric bacterium that causes several gastric disorders and accounts for 90% of all diagnosed gastric cancers (5<sup>th</sup> most common & 4<sup>th</sup> deadliest worldwide)<sup>1-3</sup>. AMPs immobilization onto biomaterials overcomes the drawbacks usually associated with their performance *in vivo*, as it avoids their proteolytic degradation and aggregation with proteins, enhancing the bactericidal effect as they become effective at concentrations lower than in solution<sup>4</sup>.

Here, a versatile, cost-effective, and environmentally friendly “one-pot” microfluidics system suitable for nanoparticles (NPs) production and bioconjugation of any ligand containing a thiol group (e.g., cysteine amino acid) is proposed. MSI-78A was directly grafted onto chitosan nanoparticles (AMP-NP, 113 ± 2 nm) surface using a microfluidic system that allows peptide bioconjugation *in situ* using the Thiol–Norbornene “Photoclick” Chemistry. The reaction yield was ~40% (analysis of amino acids - direct method), and grafting was confirmed by Fourier-transform infrared spectroscopy (FTIR), where the characteristic absorption bands of the AMP appeared at 1660 cm<sup>-1</sup> (amide I) and 1530 cm<sup>-1</sup> (amide II).

AMP-NP (10<sup>11</sup> NP/mL) had a fast-bactericidal effect against Hp 26695 strain, reaching full eradication in 30min, while for the Hp J99 strain, the same bactericidal effect was achieved after 24h. These results demonstrated that MSI-78A maintained its activity after surface grafted onto NP, in which the amount of grafted peptide (96 µg/mL) was lower than the minimal inhibitory concentration (MIC) & minimal bactericidal concentration (MBC) of the free peptide (256 µg/mL). The high Hp–chitosan affinity could further improve the killing effect. After exposure to AMP (AMP-NP), Hp membrane presented irregularities, the formation of vesicles and changes/release in the cytoplasm.

Furthermore, AMP-NP at bactericidal concentration were cytocompatible against human gastric adenocarcinoma cell lines (AGS & MKN74. ATCC®), in accordance with ISO 10,993–5;12.

Overall, the designed AMP-NPs boosted the activity of MSI-78A and are promising for Hp eradication.

Also, a straightforward system to obtain AMP-conjugated chitosan nanoparticles was developed. Its main advantage is the possibility to simultaneously produce, crosslink and immobilize different thiolated-compounds (due to thiol-ene chemistry) in the same device. This system can be further explored with other biomaterials and for different applications.

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## Nafion-based micromotors in water: fundamentals and collective motion

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The development of micro/nanomachines which can move controllably and autonomously in a fluid while carrying out targeted tasks is one of the current challenges of nanoscience and nanotechnology [1]. Many self-powered devices have been developed in recent years either as motors (in a free-standing configuration) or micropumps (immobilized on substrates). Among them, motors (also termed swimmers) that are self-propelled by chemical processes have attracted significant attention for their potential use in relevant areas such as biomedicine and water remediation. However, most of the devices developed so far are typically activated by toxic chemicals, which strongly hinders their applicability or cannot work at high salt concentrations. Among the different explored mechanisms to achieve chemical self-propulsion, ion exchange has emerged as a valuable strategy, with the significant advantage of using innocuous salts as fuels and being able to work under biologically relevant conditions. Recently, micropumps of the ion-exchanger Nafion polymer have been prepared that are capable to trigger interfacial electro-osmotic flows in water induced by chemical gradients with the subsequent local generation of electric fields [2]. Nafion is a well-known material and widely used in application areas such as fuel cells, biosensors, filtration/separation/purification technologies, antifouling coatings, etc. These Nafion micropumps can work in a wide range of salt concentrations, are activated using different cations, including heavy metal ions, and can be regenerated for reusability, showing their potentialities for effective and fast water purification strategies for environmental remediation. Note that that pumping is self-driven by the own contaminant ions. By properly nanostructuring Nafion into microarrays and tuning the surrounding surface zeta potentials, it is also possible to redirect electro-osmotic flows into unidirectional pumping [3]. Exploiting the same ion-exchange based propulsion mechanism, we have recently succeeded in the high throughput fabrication of Nafion-based micromotors using colloidal lithography and reaction ion etching. We will report on the collective behaviour of Nafion-based micromotors under crowding in water. Nafion swimmers tend to self-assemble under motion into flocks, increasing their collective velocity upon assembly, as compared to those of individual motors. The chemical gradients and interfacial fluid flows generated at the moving flock attract other micro/nanoobjects toward the flock. The attraction and trapping capacity of micro/nano-objects has been evaluated with passive polystyrene microparticles. The high trapping efficiency of these Nafion-based micromotors flocks may open the door to their future use for microplastic scavenging in water.

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## Inhibition of Catalytic Electron Transfer by Coulomb Blockade in Small Au Nanoparticles

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### Abstract

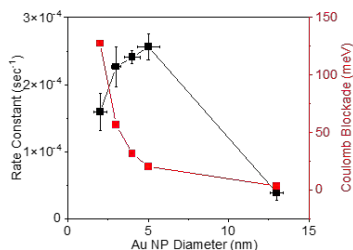
Colloidal noble metal nanoparticles (NPs) are an emerging research topic in the field of nanotechnology because of their interesting catalytic properties.<sup>1</sup> They can actively participate in redox chemical reactions and are therefore attractive for various oxidation and reduction reactions including CO<sub>2</sub> reduction, H<sub>2</sub> dissociation, and so on. The metal NPs provide alternative reaction pathways, thereby significantly reducing the activation energies for these chemical conversions. There are several strategies to reduce the activation energies for these catalytic reactions, such as by changing the size, shape, and composition of the NPs and also by changing the reaction conditions.<sup>2</sup>

To investigate the reaction mechanism of sub-10 nm Au NPs of different sizes, we have used ferricyanide (Fe<sup>3+</sup>) to ferrocyanide (Fe<sup>2+</sup>) 1-electron transfer as a model reaction system.<sup>3</sup> We have found that the reaction rate significantly depends on the size of the NPs, and the highest reaction rate was achieved in presence of Au NP with a diameter of 5 nm. We also compared the reaction rate of Fe<sup>3+</sup> to Fe<sup>2+</sup> conversion in the presence and absence of a reducing agent triethanol amine (TEOA). It has been found that the reaction pathway is significantly altered with and without TEOA. TEOA, in general, transfers the electron to Au NP and causes a negative charging of the Au NP surface. However, when the size of the NPs is very small and especially below 5 nm, the negative charging of Au NPs is inhibited by the Coulomb Blockade effect. As a result, the catalytic electron transfer from Au NP to Fe<sup>3+</sup> is also inhibited, thereby, decreasing the overall Fe<sup>3+</sup> reduction rate. These experimental findings along with theoretical calculations will help the research community in designing novel metal NPs with better catalytic properties, which will open up new possibilities for various catalytic processes for environmental remediations.

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### Figures



**Fig 1.** Catalytic rate constants of Fe<sup>3+</sup> to Fe<sup>2+</sup> reduction by different Au NPs with the diameter ranging from 2-13 nm. The calculated Coulomb Blockade energies are also plotted on the same graph for relative comparison.

## QCMD as a tool for advancing the understanding and application of nanoporous films

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The AWSensors team specializes in the Quartz Crystal Microbalance with Dissipation (QCMD) technique and focuses on the continuous development of the technology and its uses in different areas of knowledge. As it is, QCMD is a powerful tool for studying processes occurring at or near surfaces, or within thin films.

QCMD is a versatile and sensitive technique that can be applied to a wide range of nanoporous materials, such as zeolites, metal-organic frameworks, polymers, and biomaterials. By using QCMD, one can obtain information about the porosity, permeability, swelling, and hydration of nanoporous materials, as well as their adsorption and desorption kinetics and thermodynamics.

Furthermore, QCMD is a powerful tool for studying the interactions of molecules with mesoporous materials and for developing novel sensors and biosensors based on this technology. By combining QCMD with mesoporous surfaces one can achieve enhanced sensitivity and selectivity for various applications, such as biosensing, catalysis, and gas separation.

A proof of concept for the development of novel sensors and biosensors based on the QCMD technology and its combination with mesoporous sensing layers will be discussed, as well as its possibilities for reaching lower limits of detection based on a strategy of acoustic amplification.

## Nanostructure strategies towards performance-enhanced perovskite solar cells

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Organic-inorganic hybrid perovskite solar cells have attracted much attention due to their high power conversion efficiency (>23%) and low-cost fabrication. Directions to further improve these solar cells include strategies to enhance their stability and their efficiency by modifying either the perovskite absorber layer or the electron/hole transport layer. For example, the transparent electron transport layer (ETL) can be an important tuning knob influencing the charge extraction, [1] light harvesting, [2] and stability [3] in these solar cells, or the use of up-conversion nanoparticles to get better performance in the near IR part of the visible spectrum. [4] Here we present two strategies based on nanostructuration, first a fundamental study of upconversion fluorescence enhancement effects near Au nanodisks by scanning near-field optical microscopy and second the effects of a nanocolumnar TiO<sub>2</sub> layer on the performance and the stability of Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> perovskite solar cells. For the first case, the enhancement and localization of light near the metallic structures are directly visualized by using a single Er/Yb-codoped fluorescent nanocrystal glued at the end of a sharp scanning tip. [5] For the second we find that, compared to devices with planar TiO<sub>2</sub> ETLs, the TiO<sub>2</sub> nanocolumns can significantly enhance the power conversion efficiency of the perovskite solar cells by 17 % and prolong their shelf life. By analyzing the optical properties, solar cells characteristics, as well as transport/recombination properties by impedance spectroscopy, we observed light-trapping and reduced carrier recombination in solar cells associated with the use of TiO<sub>2</sub> nanocolumn arrays. [6]

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## State of the art of scientific instrumentation: from Nanocharacterization to Nanofabrication

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Izasa Scientific has long history providing scientific instrumentation to researchers, specially in the field of Nanocharacterization. Recently, we have also done an important investment to be a reference in the field of Nanofabrication.

Nanofabrication and nanocharacterization are dynamic fields that are continually pushing the boundaries of research. These technologies are rapidly evolving and play a critical role in the development of different applications across various industries. During this talk we will provide a comprehensive overview of the latest trends in nanofabrication and characterization.

The talk is specifically designed for researchers who are eager to stay updated with the latest advancements in nanofabrication and nanocharacterization. Attendees will gain valuable insights into state-of-the-art techniques, applications, and challenges in these fields, and how they can leverage these advancements in their own research for pushing the boundaries of nanotechnology research.

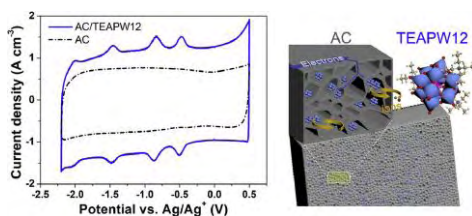
## Use of polyoxometalates-based nanomaterials for high energy density hybrid supercapacitors

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Supercapacitors, one electrochemical energy storage device (EES), have become fascinating devices due to their high power, low cost, long cycling performance and fast charge/discharge rates. However, their energy density needs to be improved to compete with other ESS in the market, especially with batteries such Li-ion technologies.[1] The development of hybrid electrodes by means of combining different nanomaterials is one of the strategies to enhance the energy density of supercapacitors. In this sense, the properties of faradaic redox-active nanomaterials and purely double-layer capacitive nanocarbons are integrated into the same electrode.[2] Moreover, the combination in the same device one capacitive electrode and a faradaic one is another possible hybridization method to increase the performance, such as in the case of metal-ion supercapacitors ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Zn}^{2+}$ ). Zn-ion is one of the chemistries that has increased its impact on the development of novel and greener energy storage devices, to zinc's low-cost, abundance and water compatibility and for this reason, has been considered as anode in hybrid devices.[3] Polyoxometalates (POMs) are well-suited redox-active nanomaterials (nanoscale metal oxide clusters from Mo, W, and V) that can perform fast reversible redox reactions without changing their structural stability,[4] providing an increase of capacity and cyclability when they are combined with nanocarbons such as activated carbon [2] or graphene oxide, [5] or inorganic 2D materials such as MXenes.[6] MXene materials has a very high volumetric capacitance, which combined with nanocarbons, which has high gravimetric capacitance, and POMs in a triple hybrid electrode shows better capacitance (87 F/g) with 1.5 times higher volumetric capacitance than those of MXenes alone. [7]



**Figure 1:** Left: CV from AC and AC/POM (TEAPW12) in acetonitrile showing an improvement on capacitance due to POM incorporation. Right: incorporation of POM in AC drawing.[2]

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## Understanding the Temperature Dependence of the Gap in Bulk and Nanocrystalline Hybrid Perovskites

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The popular use of hydrostatic pressure in optical studies of materials is partly due to the fact that a lattice-constant variation by a few percent has a large impact on the electronic band structure and thus on the optical properties. For hybrid organic/inorganic lead halide perovskites the use of optical spectroscopy techniques like photoluminescence (PL), combining experiments as a function of temperature and pressure, has led, for instance, to a deeper understanding of the atypical temperature dependence of their fundamental gap [1]. For the archetypal perovskite MAPbI<sub>3</sub> (MA stands for methylammonium) it is shown that the variation of the gap with temperature is due to an almost equal footing of thermal expansion and electron-phonon interaction effects [2]. This result seems to possess general validity, holding also for the tetragonal or cubic phases, stable at ambient conditions, of most halide perovskite counterparts. As an example, recent results obtained for MA rich FA<sub>x</sub>MA<sub>1-x</sub>PbI<sub>3</sub> solid solutions, where FA stands for formamidinium, will be presented [3]. Finally, evidence of a size-dependent enhancement of the electron-phonon contribution to the temperature-induced renormalization of the gap in MAPbI<sub>3</sub> nanocrystals (NCs) will be provided [4]. Interestingly, it is found that as the NC size decreases, the electron-phonon contribution gains in importance, gradually increasing from ca. 50% as in bulk to about 75% for NCs of a few nanometers in diameter. In all these cases, the outcome from high-pressure PL experiments was crucial for the quantitative assessment of the weight of the electron-phonon interaction relative to thermal expansion, as far as the temperature dependence of the fundamental gap of hybrid perovskites is concerned.

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### Figures

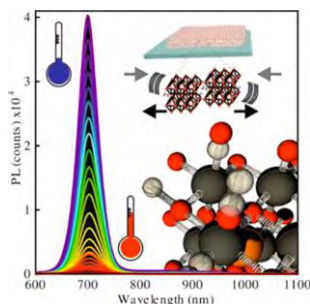


Figure 1: Temperature dependence of the photoluminescence in MAPbI<sub>3</sub> nanocrystals.

## Hybrid inorganic-organic biofunctional materials for biofabrication

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Biofunctional materials can be designed to offer an stimuli-responsive behaviour presenting several advances and alternatives to mimic as realistic as possible biological systems. The exact reproduction of the forces and stimuli that occur in the human body is still a challenge, however by the combination of hybrid inorganic-organic materials similar effects can be achieved.<sup>[1]</sup> Moreover, understanding what happens in a complex biological system over time, is of great interest. By the incorporation of inorganic nanoparticles (NPs) into the system that can respond to externally applied physical changes, some of these goals can be achieved. Our focus is therefore, on the synthesis of hybrid inks containing NPs and functional polymers, which can be printed with high resolution 3D printing techniques and provide a desired response upon activation. This enables us not only to control spatial resolution on a micro-scale and deposit multiple different inks in close proximity, but also fabricate responsive in vitro models of pathological interests.<sup>[2]</sup> Thus, we aim to create different models capable of reproducing different physiologically relevant events. For example, we have developed different scaffolds to support tumor growth and evaluated their evolution thanks to hybrid materials.<sup>[3,4]</sup> We are also working on the fabrication of an artery model, which consists of 3D printed layers including endothelial and smooth muscle cells. In addition, we are working on the fabrication of pulmonary models, specifically on the fabrication of an alveoli wall model representing the air-blood interface which can remodel breathing forces. Developing these advanced hybrid materials implies improvements in cell engineering techniques, in material designs, as well as advanced imaging tools to accurately characterize them. To address this, we are exploring methods to improve imaging resolution and speed, using the hybrid NPs included into the model which can also act as contrast agents for correlative imaging techniques.<sup>[5-7]</sup> These sophisticated models offer many advantages over current materials and techniques in biomedical applications.

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## Tuneable Work Function of SnO<sub>2</sub> and TiO<sub>2</sub> Nanomaterials: Challenges and Applications

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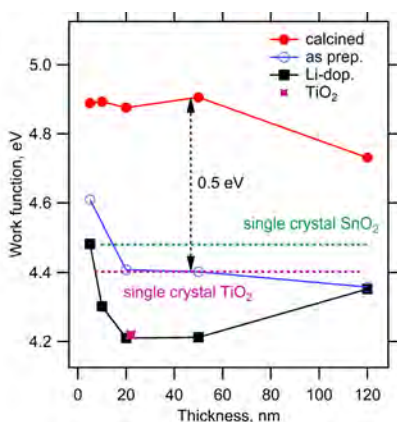
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The work function ( $\phi$ ) of nanomaterials and thin films based on oxide semiconductors (SnO<sub>2</sub> or TiO<sub>2</sub>) is one of the key parameters controlling their use in energy applications, such as perovskite photovoltaics, photocatalysis, solar fuel generation and Li-batteries [1]. Yet the determination of  $\phi$  by photoelectron spectroscopy (XPS, UPS, including NAP-techniques), photocurrent onset potential, Kelvin probe measurements (including KPFM) and electrochemical impedance spectroscopy is challenging, sometimes even impossible for fundamental reasons (e.g. in some nano-porous thin films) [2]. Inconsistent data from various experimental and theoretical works provoked conflicting debate in the literature [3]. We have addressed these contradictions by detailed analysis, tailored materials' syntheses and interface engineering. We found that the work function of ALD-grown SnO<sub>2</sub> is easily tuneable in a broad range of ca. 0.7 eV by the film thickness, calcination or doping (Fig. 1). On the other hand, the work function of ALD-grown TiO<sub>2</sub> is nearly unchanged by calcination, but still markedly smaller than the value of anatase single crystal [2]. Furthermore, TiO<sub>2</sub> thin film is much more sensitive to thermal cracking as compared to SnO<sub>2</sub>. This knowledge provides rationale for optimization of oxide semiconductors for various technologies of energy conversion and storage. Acknowledgement: This work was supported by the Grant Agency of the Czech Republic (contract No. 22-24138S).

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**Figure 1:** The work function from Kelvin probe measurements on the ALD-grown SnO<sub>2</sub> films of varying thicknesses. Blue: as-prepared (quasi-amorphous) films. Red: calcined at 450°C in air. Black: subjected to electrochemical doping with Li. The work function of ALD-TiO<sub>2</sub> is shown by magenta star (22 nm film, as prepared or calcined). Green and magenta dashed lines indicate the values for SnO<sub>2</sub> cassiterite (001) and TiO<sub>2</sub> anatase (101) single-crystals, respectively.

## Influence of the Ablation Liquid on the Phase and Magnetization of Laser-generated Fe-Ni Nanoparticles

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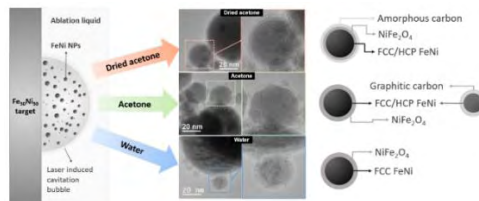
### Abstract

Fe<sub>50</sub>Ni<sub>50</sub> nanoparticles are employed in biomedicine, catalysis, and magnetic actuators due to their soft magnetic response and large magnetization. However, the nanoparticles' properties are determined by the material phase (FCC, HCP, L1<sub>0</sub>), alloy composition, as well as core-shell structure. Pulsed laser ablation in liquid (PLAL) allows the synthesis of high-purity colloidal alloy nanoparticles by ablating a bulk alloy target in a selected solvent. The modification of the ablation solvent can alter the core-shell structure of the generated nanoparticles, and, as a result, provides the opportunity to tune their properties. Organic solvents are usually preferred to minimize nanoparticle oxidation, but economical laboratory and technical grade solvents contain water impurities, which is a potential source of oxidation. In this study, we investigated the influence of water impurity in acetone by using molecular sieves (3 Å) to capture water molecules and compared the properties of the generated Fe<sub>50</sub>Ni<sub>50</sub> nanoparticles with the nanoparticles produced in acetone without molecular sieves treatment and Milli-Q (deionized) water. Our investigation showed that the nanoparticles' size, crystallographic phases, core-shell structure, oxidation level, and the magnetization of Fe<sub>50</sub>Ni<sub>50</sub> nanoparticles produced by PLAL are influenced by the water content in acetone. XRD synchrotron analysis revealed that the high-pressure HCP FeNi phase was found in the sample produced in acetone and dried acetone, but not in water. Mössbauer spectroscopy showed that the FeNi NPs oxidation in dried acetone is reduced by 8% compared to acetone. The saturation magnetization value of Fe<sub>50</sub>Ni<sub>50</sub> ablated in water is the highest, 68 Am<sup>2</sup>/kg, followed by ablation in dried acetone, 59 Am<sup>2</sup>/kg, and in acetone, 52 Am<sup>2</sup>/kg. The core-shell formation in these three liquids is also a distinctive feature of the solvent (Fig. 1), opening the possibility to tune the core-shell structure by reducing water impurity in the organic solvent [1].

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### Figures



**Figure 1:** Schematic illustration of laser-ablated FeNi NPs in various liquids. The formation of diverse core@shell structures can be observed depending on the ablation liquid; FCC/HCP FeNi@NiFe<sub>2</sub>O<sub>4</sub>@amorphous carbon in dried acetone, FCC/HCP FeNi@NiFe<sub>2</sub>O<sub>4</sub> and FCC/HCP FeNi@graphitic carbon in acetone, and FCC FeNi@NiFe<sub>2</sub>O<sub>4</sub> in deionized water.

## Exploring the Potential of 2D-based Nano/Microswimmers for Biomedical and Environmental Applications

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### Abstract

Nano/microswimmers with autonomous motion are the frontier of nanotechnology and nanomaterial research. These self-propelled nano/microswimmers convert chemical energy obtained from their surroundings to propulsion. Particularly, the recent progress in targeted drug delivery and efficient water purification systems is very promising. Graphene and the recently discovered layered materials -beyond graphene- have superior properties and have made a great impact on the new generation of energy, biomedical and environmental applications. Integration of single/few layers materials with extremely high surface area into nano/microswimmers has been created a dynamic platform which could significantly enhance motor's functions in terms of adsorption capacity and mobility. We have employed 2D-based microswimmers to demonstrate (i) organics / heavy metals / ions collection and DOX loading, (ii) a targeted transport system, (iii) the on-demand release mechanism, and (iv) the recovery of the robots for further usage.<sup>[1-13]</sup>

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## DFT study of nanoporous graphene filled by heteroatoms as catalysts

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Graphene exhibits a low chemical reactivity that limits its electrocatalytic applications. But, according to the reports published, the substitution of C atoms in graphene's lattice with B and N atoms is an efficient way to enhance its chemical reaction [1][2]. However, a step further in the efficiency could be achieved by controlling the distribution of the dopants all along the membrane.

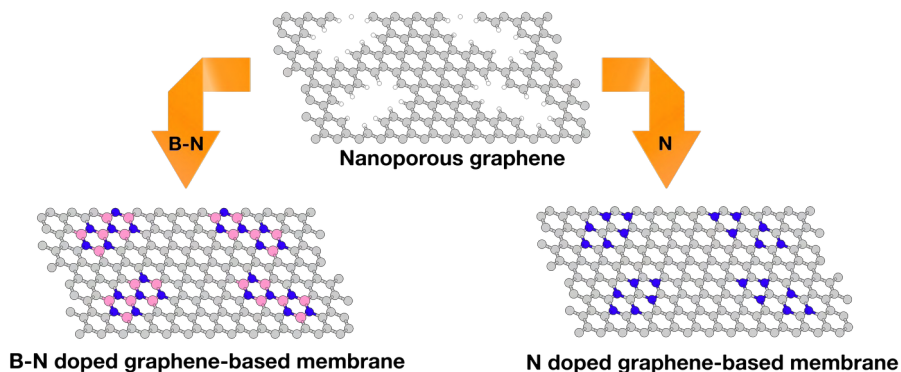
In this work, we propose to use the nanoporous graphene (NPG) obtained by Moreno et al. [3] as a template to obtain a heteroatom-doped graphene membrane with equal active sites that are evenly distributed in the lattice. For that, we propose to fill the regular pores of the atomically precise 2D carbon-based material with triazine and borazine molecules.

By employing Density Functional Theory (DFT) the resulting heteroatom doped graphene-based membranes have been characterized by analyzing their electronic properties. Furthermore, to test how the chemical reactivity of these dopants improves graphene's reactivity, we have also investigated the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) catalyzed by these materials. Our results for CO<sub>2</sub>RR pave the way to explore other interesting reactions, e.g., the oxygen evolution reaction (OER).

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### Figures



**Figure 1:** Filling of the pores in NPG to obtain heteroatom-doped based membranes.

## Optimal spin-orbit torque in graphene-based devices

Joaquín Medina Dueñas, José H. García, Stephan Roche

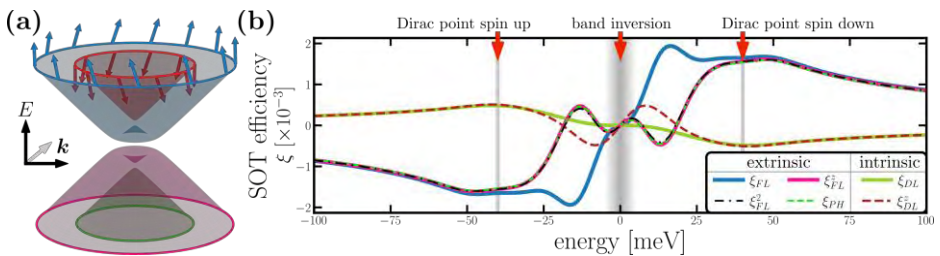
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Current magnetic non-volatile memories are mainly limited by inefficient charge injection and magnet-magnet interactions. Both limitations may be overcome by replacing one magnet with a strong spin-orbit coupling (SOC) material, which acts as a current-driven spin source to control the state of the remaining magnet. Such a device is known as a spin-orbit torque (SOT) magnetic memory, and presents a major breakthrough in energy efficiency[1]. Tunable magnetic and SOC properties via proximity effects have earned graphene-based van der Waals heterostructures major attention as an efficient spintronic platform[2]. In this work we perform an extensive analysis on the SOT mechanisms in graphene with proximity-induced SOC and magnetism. We demonstrate that, in addition to the conventional field-like and damping-like torques, four non-conventional torque contributions of sizable magnitude are relevant to the magnetisation dynamics. We study the physical origin of the torques unveiling an essential role of spin-pseudospin entanglement. Our theoretical developments are supported by quantum transport simulations of large-scale devices including disorder. Our results consolidate graphene as a promising platform for magnetic memories and provides a robust path to experimentally achieving optimal spin-orbit torque.

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### Figures



**Figure 1:** SOT in graphene with proximity-induced SOC and magnetisation. (a) Scheme for the dispersion of the system. The magnetisation shifts the Dirac points for spin up/down bands in opposite energies, with a band inversion at the charge neutrality point due to Rashba SOC. Spin texture depicted by coloured arrows. (b) The SOT efficiency exhibits a non-trivial behaviour with respect to the Fermi level. Close to the band inversion the system is dominated by spin-pseudospin entanglement. In this region the torque is highly tunable, and an optimal for the conventional field-like torque emerges.

## Device to materials pathway for electron traps detection in amorphous GeSe-based selector

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Choosing the ideal material employed in selector devices is a challenging task from the theoretical and experimental side [1], mainly due to the need for a synergistic approach between techniques. We propose a material-to-device multiscale technique [2] (including experiments, device modelling, and atomistic simulations) that extracts traps/defects characteristics from the experimental device electrical data and connect them to the microscopic properties of the materials (atomic defect), in a learning that correlates the electrical properties of the specific device to the electronic properties. We use this material-to-device multiscale technique for the efficient characterization of active traps of amorphous GeSe chalcogenides, being able to trace back the specific features of materials responsible for the measured findings and to connect them with an atomistic description of the sample. We will describe the overall approach, focusing on the Density Functional Theory calculations that are part of this workflow. We find that hole and electron trap states have different characteristics: the former do not exhibit the presence of homopolar Ge-Ge bonds that are, instead, a common feature of the latter. Our combined approach can be applied to other materials and devices, which is very beneficial for the efficient development and optimization of existing and novel technologies.

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## Enhancement Strategies for Stability and Efficiency of Perovskite Solar Cells

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### Abstract

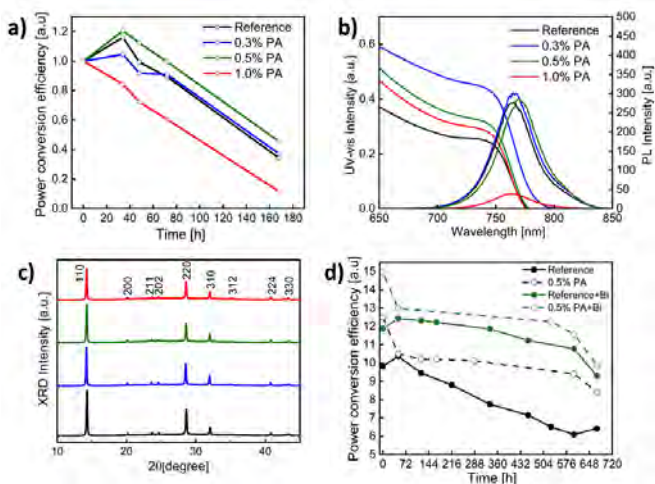
Perovskite solar cells (PSCs) have attracted considerable attention in the photovoltaic (PV) field due to the rapid enhancement in their power conversion efficiency (PCE). PSCs have several advantages, such as, high absorption coefficient, tuneable bandgap, and low-cost materials and fabrication procedures.[1] However, long-term stability is still the main problem in avoiding PSCs reaching commercialization stage. The  $I^-$  and  $MA^+$  ions can migrate causing irreversible PV device degradation. In this work, we use of propionic acid ( $CH_3CH_2COOH$ , PA), with distinct PA/MAPbI<sub>3</sub> ratios, to dope methylammonium lead iodide (MAPbI<sub>3</sub>) perovskite thin films for avoiding ions migration. [2] Once the optimal ratio is chosen, a thin but compact Bismuth (Bi) interlayer was evaporated between electron transport layer and top electrode for protecting it from iodine corrosion.[3] Figure 1. a) and d) demonstrate that PSC fabricated with the 0.5 wt% doped MAPbI<sub>3</sub> perovskite film and Bi interlayer results in better PCE and are more stable over time than the other manufactured devices. Figure 1 b) and c) exhibit how to influence the amount of PA in the optoelectronic and structural properties of MAPbI<sub>3</sub> perovskite thin film.

**Acknowledgements:** This work was supported by the Ministerio de Universidades of Spain, NextGenerationEU, Plan de Recuperación, Transformación y Resiliencia, Colombia Scientific Program within the framework of the call Ecosistema Científico (Contract FP44842-218-2018), MICINN/FEDER, PDI2021-128342OB-I00, AGAUR ref. 2021-SGR-00739, and ICREA under the ICREA Academia Award.

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### Figures



**Figure 1:** PCE evolution plots vs. time of a) perovskite films with different PA/MAPbI<sub>3</sub> ratios and d) with the Bi interlayer addition. b) XRD diffractogram and c) UV-vis absorption and photoluminescence emission spectra images of the perovskite films with different PA/MAPbI<sub>3</sub> ratios.

## Diverse morphologies of amorphous nanostructures by electrospaying

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Electrospray is a liquid atomization technique of interest in diverse applications. For example, it is capable of producing nano- to micro-particles with biomedical and pharmaceutical functions (Boda et al., 2018). A precursor solution is fed through the exit of an electrified capillary where it forms a Taylor cone meniscus, which emits a thin liquid jet (Rosell-Llompart et al., 2018). The electrical charge allows overcoming surface tension forces and thus produce tiny structures. Different scenarios produce different morphologies. The jet tends to break up into droplets that become particles after the solvent evaporates. The charged droplets have initially repeatable sizes, but later, after some solvent evaporation, they can undergo Coulombic instabilities (CIs), leading to progeny submicrometric particles (Bodnár et al., 2018). On the other hand, the jet breakup may be incomplete for high solution viscosity. In this case, thin nanofilaments remain between the particles. Only general understanding exists on these regimes and on the roles played by the different many (process, solution, ambient) variables. Here, we present systematic research aimed at clarifying those roles, more specifically, how the morphologies depend on the solution physico-chemical properties such as viscosity and electrical conductivity, while varying solute concentration and molecular weight (MW).

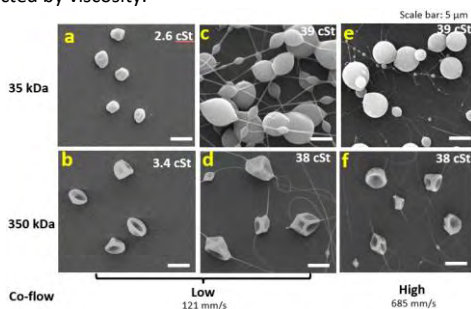
With very dilute polystyrene (PS) in butanone (MEK) solutions, CIs arise and progeny particles are visible. With increased concentration, progeny particles disappear, while size-monodisperse globular main particles form (Figs. 1a, 1b), as well as satellite particles at the periphery of the collection (not shown). Further rising the solution viscosity, the collected residues are linked by filaments (Figs. 1c, 1d) due to incomplete jet breakup. High solution viscosity with low electrical conductivity led to incomplete jet breakup; so, it became critical to use a solvent-saturated gas co-flow for highly viscous solutions to prevent drying of the Taylor cone and obtain stable electrospaying. We also found that the filaments get thinner when the co-flow speed around the Taylor cone is increased, as shown in Figs. 1e and 1f for the same solutions as in Figs. 1c and 1d, respectively. The sizes of the particles remained nearly unchanged by the co-flow increase. Particles with low MW are spherical whereas, high MW forms deflated shells. Blended solutions produced particles with in-between shapes. For different molecular weights, the boundary between these regimes correlated is predicted by viscosity.

### Acknowledgments

The Spanish Government and the EU (under grants PGC2018-099687-B-I00, PID2021-129064 NB-I00, and FPU19/03733 scholarship), the Catalan Gov. under grant 2021SGR-00978, the EU's Horizon 2020 program under Marie Skłodowska-Curie grant agreement No. 945413 and by the Univ. Rovira i Virgili.

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**Figure 1:** Electrospayed particles from PS/MEK solutions at: (a) 15, (b) 5, (c) 40, (d) 14 wt.%, with low co-flow, and (e) 40, (f) 14 wt.%, both with high co-flow. Left panels are for Mw 35 kDa PS, right ones for 350 kDa. Top panels show the solution viscosity (at 22°C).

## Nanosized hydrogel dots for biomarker detection

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Hydrogels are interesting materials for biosensing applications. Their tridimensional nature and high water content make them an appropriate matrix for protein immobilization, while their inertness minimizes non-specific protein binding<sup>1</sup>. Hydrogels also offer the possibility to produce protein microarrays on non-functionalized substrates, in a cost-efficient way<sup>2</sup>.

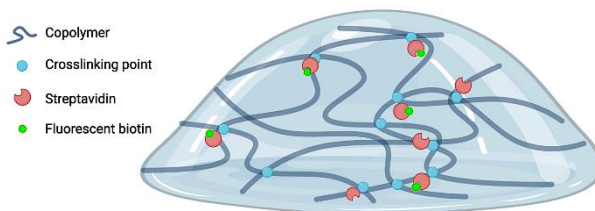
Here in this study we present a model for a biomarker sensor based on spotted picoliter-volume hydrogel drops with a thickness of few nanometers. The polymer contains photoreactive moieties, allowing for UV crosslinking after deposition of the dots on the substrate. In the same reaction, the polymer network was crosslinked and adhered to the substrate. When streptavidin was mixed with the polymer, the protein was immobilized in the matrix upon UV-crosslinking. In the first stages, the optimal crosslinking parameters were studied, and dot morphology was characterized with AFM and SEM.

For the proof of concept of the biosensing application, the streptavidin-biotin interaction was used to model an antibody-antigen interaction, and fluorescence was used for protein detection. In a first approach, the immobilization of streptavidin in the hydrogel matrix was studied using fluorochrome-tagged streptavidin. Then, regular streptavidin was immobilized and the functionalized dots were incubated with fluorescent biotin. The detection of fluorescence indicates that the streptavidin-biotin interaction has taken place. An analysis algorithm was developed which allows to discriminate fluorescence coming from the hydrogel dot and from the polymeric substrate, eliminating non-specific fluorescence from the analysis.

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### Figures



**Figure 1:** Representation of the experimental design. The hydrogel dots contain immobilized streptavidin, which is detected by binding of fluorescent biotin.

## Development of multifunctional micro/nanoparticles for environmental remediation

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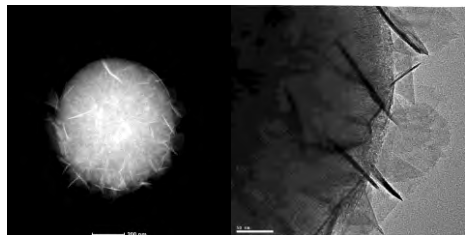
Remediation of wastewater has become a great challenge to face worldwide, it is included as one of the goals for the 2030 ONU Agenda to achieve universal and equitable access to safe and affordable drinking water for all <sup>1</sup>. Although there are several mechanisms to degrade pollutants from water, photocatalysis is a simpler, more sustainable, and cost-effective water treatment technology that uses light and no additional reactants to mineralize toxic pollutants. The use of nanomaterials or nanostructured semiconductor photocatalysts has shown significant efficiency in the degradation of organic and inorganic pollutants <sup>2</sup>. Recently, new layered 2D nanomaterials based on transition metal dichalcogenides (TMDs) are featuring special attributes for photocatalysis such as low-bandgap for efficient visible light conversion energy, significant photon absorption, and band-gap tunability via modulation of the VB and CB with the number of stacked layers<sup>3,4</sup>. Also of interest is the capability to tune the layer stack growth in different orientations and exploit layer edges as highly catalytic sites for photocatalytic activity enhancement. Therefore, MoS<sub>2</sub> and MoSe<sub>2</sub> TMDs displaying such attributes can be exploited for the generation of reactive oxygen species (ROS) that are essential for the degradation of pollutants in water.

The present work aims at the development of multicomponent micro/nanoparticles by integrating TMD semiconductors as the main photocatalysts to degrade pollutants. These photocatalysts are combined with different silicon microstructures such as mesoporous particles and doped silicon wires as platforms to obtain high loading of the active TMD nanostructures. Likewise, different synthesis methods and phases of MoS<sub>2</sub> are studied, compared, and characterized. In addition, to improve ROS production and reduce the photo recombination of generated species, co-catalysts, like noble metals, other TMDs materials, and/or magnetic nanostructures are used. The photocatalyst performance is evaluated on typical dyes pollutants such as Rhodamine B and also on antibiotics such as tetracycline.

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### Figures



**Figure 1:** TEM images of Silica Particle loaded with active sites MoS<sub>2</sub>.



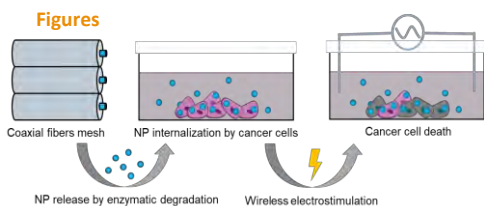
## Wireless electrostimulation nanomaterials platform for cancer treatment

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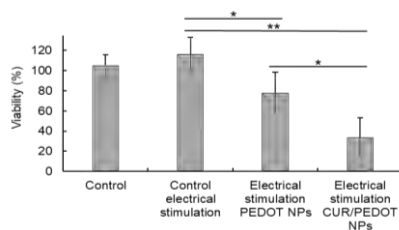
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Controlled drug delivery systems are key to develop new cancer treatment strategies, as cancer is the leading cause of death in many developed countries. The use of controlled drug delivery systems allows to provide a localized therapy and avoiding systemic toxic effects, as lower amounts of drug administration would be required. A wireless electrostimulation system was developed for the treatment of breast and prostate cancer composed of two components: poly(3,4-ethylenedioxythiophene) (PEDOT) nanoparticles (NPs) loaded with anticancer drug curcumin (CUR), encapsulated in biodegradable coaxial poly(glycerol sebacate)/poly(caprolactone) (PGS/PCL) fibers. Both NPs and fibers were fully characterized. The PEDOT NPs allowed the controlled delivery of CUR using specific applied potentials. The coaxial fibers were employed to control the systemic release of the PEDOT NPs, depending on lipolytic activity. A controlled release of CUR from NPs was achieved by electrostimulation, achieving 79% of CUR released at an electrical potential of -1.5 V. Biodegradation of the fibers was assessed using lipase, resulting in a sustained release of NPs. Wireless electrostimulation of PC-3 cancer cells using CUR/PEDOT NPs was successfully performed, resulting in 67% decrease in cancer cell viability, caused by the controlled release of CUR from the PEDOT NPs. We have successfully produced PGS/PCL coaxial fibers, with embedded electroresponsive PEDOT NPs, which were loaded with the anticancer drug CUR. PC-3 and MCF7 cancer cell lines internalized CUR/PEDOT NPs in 24h, with no perceived cell death or alterations in cell morphology in the absence of electrical stimulation. Most importantly, wireless electrostimulation of cancer cells using CUR/PEDOT NPs was successfully performed, resulting in a very significant decrease in cancer cell viability, caused by the controlled release of CUR from CUR/PEDOT NPs. Overall, our results show the potential of using wireless electrostimulation of drug-loaded NPs for cancer treatment, using safe voltages for the human body, and ensuring the delivery of the anticancer drug in a highly controlled way. Additionally, our results highlight the potential of using FDA approved materials to create a transdermal implant that would act as a reservoir of the NPs to be delivered in a sustained manner to the patient. This work is financed by national funds from FCT - Fundação para a Ciência e a Tecnologia, I.P., with dedicated funds from the project eOnco (2022.07252.PTDC) and the PhD scholarship (SFRH/BD/145057/2019) and in the scope of the project Belive (PTDC/EMD-EMD/30828/2017), iBB (UIDB/04565/2020 and UIDP/04565/2020), i4HB (LA/P/0140/2020), and project BioMaterARISES (EXPL/CTM-CTM/0995/2021).



**Figure 1:** Schematic representation of controlled release of CUR/PEDOT NPs from PGS/PCL fibers through lipolytic enzymatic activity, followed by NP internalization by cancer cells and subsequent wireless electrostimulation to promote cancer cells death.



**Figure 2:** Viability of PC-3 cells after 24 h incubation in culture medium supplemented with 50 µg/mL of either PEDOT NPs or CUR/PEDOT NPs under wireless electrical stimulation and respective controls, n=3. \*p-value<0.05; \*\*p-value<0.01

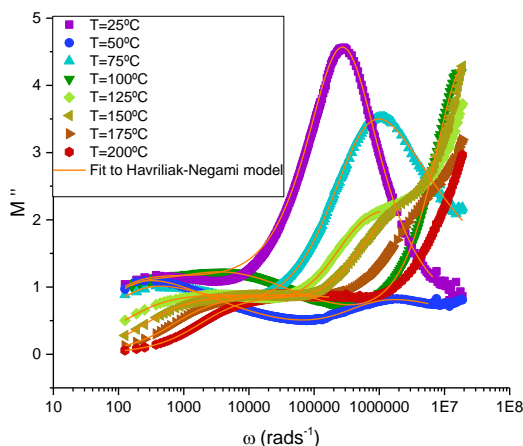
## Magnetic and dielectric properties of Electrospun $\text{LiNbO}_3\text{-CoFe}_2\text{O}_4$ Nanofibers

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Multiferroic nanostructured composites constructed by combining magnetostrictive and piezoelectric materials, possess not only ferroelectricity and ferromagnetism in each individual phase, but also exhibit a stress mediated coupling between their magnetic and electric properties, the so called magnetoelectric effect. In this context, sub-micrometer diameter electrospun nanofibers are particularly attractive, due to their low dimensionality, high aspect ratio and ease of production. By combining suitable piezoelectric and magnetostrictive compounds in the electrospinning precursor solutions, composite magnetoelectric nanofibers are achieved, with the potential to show very high coupling coefficients, broadening the prospects of potential applications. In this respect, lithium niobate ( $\text{LNO-LiNbO}_3$ ), due to its high piezoelectric, pyroelectric, electro-optical, birefringent, photorefractive and photoelastic properties, presents a rich variety of favorable properties towards applications. While cobalt ferrite ( $\text{CFO-CoFe}_2\text{O}_4$ ) presents a high magnetocrystalline anisotropy and magnetostriction, making it suitable for application in magnetoelectric composites.



**Figure 1:** Imaginary component of electric modulus of composite sample with 40% of CFO at different temperatures and analytical fit using Havriliak-Negami model.

Here, multiferroic nanofibers composed by  $\text{LiNbO}_3$  and  $\text{CoFe}_2\text{O}_4$  were synthesized through the electrospinning technique, with different CFO concentrations (x<sub>CFO</sub> from 10% to 40%). Subsequently, they were annealed at 650°C, for ~3 hours, to vaporize the transporting polymer. X-ray diffraction measurements showed that the fibers were polycrystalline, presenting the CFO cubic spinel phase and the LNO rhombohedral ferroelectric structure, as envisaged. The lattice parameters of both phases showed a distortion compared to bulk values, which was associated with the presence of the mechanical coupling interaction between them. From the scanning electron microscopy measurements (SEM) the nanofibers presented diameters in the 100-400 nanometers range.

The dielectric properties of the produced composite nanofiber samples were

determined through impedance spectroscopy, at various temperatures and frequencies. Two clear and distinct relaxations were observed at every temperature, arising from the electrical response of the LNO grains and grain boundaries. At high temperatures, a third relaxation was observed, arising from the presence of the CFO phase. The results were analyzed through fits of the experimental data to the Havriliak-Negami model (Figure 1), with the addition of an electrical conductivity contribution to the dielectric permittivity. As, such, in this work, the influence of the  $\text{CoFe}_2\text{O}_4$  concentration on the determined relaxation times, activation energies, conductive behavior and magnetization dependence will be discussed and presented.

## 2D materials by Atomic Layer Deposition: Molybdenum dichalcogenides

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The success of graphene opened a door for a new class of semiconducting 2D transition metal dichalcogenides, which have attracted considerable attention due to their layered structure, suitable band gap, electrochemically active unsaturated edges and relatively good stability against photocorrosion. These properties result promising for different applications including, hydrogen evolution reaction (HER), photocatalysis and Li-ion batteries. Apart from the widely studied 2D MoS<sub>2</sub>, 2D selenide and telluride equivalents, MoSe<sub>2</sub> and MoTe<sub>2</sub>, have recently gained considerable interest due to their higher electrical conductivity, wider inter-layer distance and narrower bandgap as compared to MoS<sub>2</sub>, high surface area and close to zero Gibbs free energy edges for hydrogen adsorption. Unlike sulfide dichalcogenides, the lack of Se and Te precursors have prevented the synthesis of selenide and telluride dichalcogenides by ALD. In order to overcome such impediment, we present a set of novel in-house synthesized Se and Te compounds, which were successfully combined with commercial Mo precursor to synthesize MoSe<sub>2</sub> and MoTe<sub>2</sub> by ALD [1-5].

The as-deposited ALD MoS<sub>2</sub>, MoSe<sub>2</sub> and MoTe<sub>2</sub> on substrates of different nature were extensively characterized by different techniques, which confirmed the chemical composition and revealed the growth of 2D flaky nano-crystalline MoS<sub>2</sub>, MoSe<sub>2</sub> and MoTe<sub>2</sub>. In parallel, MoS<sub>2</sub>, MoSe<sub>2</sub> and MoTe<sub>2</sub>@TiO<sub>2</sub> nanotube layers (TNTs) heterostructures were fabricated in a simple and fast fashion to explore and exploit the MoS<sub>2</sub>, MoSe<sub>2</sub> and MoTe<sub>2</sub> photo- and electrocatalytic properties. TNTs act as excellent photoactive supporting material providing a high surface area, unique directionality for charge separation, and highly effective charge collection. The presentation will introduce and describe the synthesis of the 2D Mo dichalcogenides, the corresponding physical and electrochemical characterization and encouraging results obtained in HER [4,5], photocatalysis [4-6] and Li-ion batteries [7].

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## High Temperature Magnetic Measurements to Investigate Semiconducting/Ferromagnetic Nanocomposites

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Porous silicon (PSi) and silicon nanotubes (SiNTs) are presented as a platform for filling with FePt nanostructures. The difference of the magnetic characteristics between the two systems is figured out. Furthermore, the FePt filled templates are compared with the same template materials filled with Ni/Co by electrodeposition.

The porous silicon is produced by anodization of a highly doped n-type silicon wafer in a 10 wt% HF solution. The produced morphology offers separated pores of about 50 nm and a mean distance between the pores of 50 nm. The SiNTs are fabricated in using an array of ZO wires as template, subsequent silicon deposition and finally etching off the ZO. The inner diameter of the tubes and also the wall thickness can be tuned by the fabrication process. In this work SiNTs with comparable inner diameter to the PSi structure and a wall of about 10 nm are used [1]. FePt nanoparticles (NPs) are deposited electroless inside the pores and the tubes, respectively whereat the molar ratio of Fe is varied. For this purpose a 3 component solution consisting of  $\text{H}_2\text{PtCl}_6$ ,  $\text{Fe}(\text{NO}_3)_3$  and citric acid is used, whereas the ratio of the components is modified.

Ni and Co, both metals are electrodeposited within the nanostructured silicon in using aqueous  $\text{NiSO}_4$  and  $\text{CoSO}_4$  solutions by applying a current density of  $15 \text{ mA/cm}^2$  and a frequency of 0.1 Hz.

The varying magnetic response of the different composite systems, porous silicon and silicon nanotubes is investigated. PSi/FePt shows a higher coercivity and remanence than SiNTs/FePt and thus a higher hard magnetic performance. The variation of the coercivities between SiNTs/FePt and PSi/FePt is about 57%.

Considering the FePt deposits with different molar ratio of Fe the coercivities vary in a range of 5% in the case of both template types. Comparing FePt loaded samples with Co loaded samples in all cases an increase of the coercivity and of the remanence is observed for FePt, whereat in the case of PSi as template material the increase is significantly stronger than in the case of SiNTs samples. Figure 1 shows the comparison of the hysteresis of PSi and SiNTs filled with FePt NPs.

Beside low temperature and room temperature magnetic measurements, the magnetic behavior of the samples is investigated at high temperatures up to 1273 K.

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### Figures

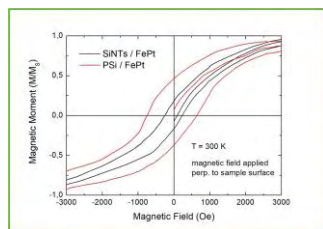


Figure 2: Hysteresis curves of PSi (red line) and SiNTs filled with FePt NPs.

## In-situ growth of zinc oxide nanoparticles within porous nanocellulose films

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Our society faces an everyday technological evolution, where industries now need to meet a balance between faster, smaller and more sustainable electronics. Sustainability can be achieved not only by facilitating the disposal or recycling of the electronic equipment, as well as by making them energetically self-sufficient [1]. This can be carried-out by combining energy harvesting techniques with biopolymers to produce nanosensors or nanogenerators. Cellulose is the most abundant polymer on earth and an obvious candidate for bioelectronics purposes. While nanocellulose has the benefit of combining cellulose's properties with the high surface area of nanomaterials, its processing requires harsh conditions and energy expenditure. Bacterial nanocellulose (BC) is an eco-friendlier material, being produced in pure form by microorganisms, and being a great substrate to hold active materials, like conductive or piezoelectric nanostructures [2]. Piezoelectricity is the conversion of mechanical energy into electrical energy, and zinc oxide (ZnO) is an example of a metal oxide that presents this behaviour. It is a sustainable semiconductor oxide, with easy synthesis routes, and good biocompatibility [3].

In this work we have produced BC films filled with ZnO nanoparticles for piezoelectric purposes. The ZnO nanoparticles were grown in situ through a microwave assisted hydrothermal synthesis and the films were washed through several cycles and characterized by XRD, Raman, SEM, TEM, UV-Vis and FTIR. The mechanical, thermic and electric characterization, namely the piezoelectric properties at the nanoscale, were also measured. The structural-functional properties relation will be fully presented and discussed.

**Acknowledgements:** This work was developed under the scope of the CICECO-Aveiro. Projects: FCT (UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020); NANOTRONICS (IF/300/2015) and FLEXIDEVICE ((PTDC/CTM-CTM/29671/2017). FS also thanks FCT for the PhD grant SFRH/BD/150787/2020 and COST CA20126 for STSM grant.

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## Development of porous microwave-acid treated sepiolite /ZnO nanocomposite particles for potential ethylene scavenger application

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Ethylene scavengers have been used to adsorb or decompose ethylene, a phytohormone responsible for inducing biochemical, physiological, and structural changes during the fruit ripening, in order to prolong the fruit shelf-life [1]. Natural porous clays, such as sepiolite, have been addressed as ethylene adsorbing matrices [2]. However, their low adsorption activity still compromise their broad application. Recently, an acid treatment of natural clays has been applied to increase their porosity [3]. On the other hand, ZnO has already demonstrated to have ethylene chemisorption activity [4]. Combination of acid treated clays and ZnO particles may enhance the ethylene adsorption kinetics and pave the way for different applications. In this work, the feasibility of using a microwave (MW)-assisted acid treatment to modify sepiolites and further assembling ZnO nanoparticles on their structure was explored. The influence of MW-assisted acid treatment and nano co-precipitation of ZnO on chemical, structural, morphological, and ethylene scavenging properties of sepiolite was studied. Untreated sepiolite was used as control.

Sepiolite was chemically composed of SiO<sub>2</sub> 76.7 %, MgO 7.2%, K<sub>2</sub>O 3.2%, P<sub>2</sub>O<sub>5</sub> 3.0%, CaO 2.4%, and Al<sub>2</sub>O<sub>3</sub> 1.7% (wt%). MW-acid treatment caused the depletion of Mg<sup>2+</sup> from sepiolite octahedral sheets, which was confirmed by the progressive loss of FTIR bands attributed to magnesium species coordinated with -OH and H<sub>2</sub>O, and the decrease of MgO content (3.2%) determined by X-ray fluorescence. The modification of sepiolite sheets increased its specific surface area from 337 m<sup>2</sup>/g to 519 m<sup>2</sup>/g and pore volume from 0.404 cm<sup>3</sup>/g to 0.769 cm<sup>3</sup>/g. The posterior synthesis of ZnO on MW-acid treated sepiolite surface generated sepiolite/ZnO nanocomposite particles. X-ray fluorescence confirmed the presence of 17.1% ZnO, as expected by the amount of added ZnO precursors. STEM images revealed that ZnO nanoparticles synthesized on MW-acid treated sepiolite showed a size between 1.0 nm and 2.5 nm, similar to the ones synthesized without any clay support. The assembly of ZnO decreased the specific surface area (423 m<sup>2</sup>/g) and pore volume (0.613 cm<sup>3</sup>/g) of MW-acid treated sepiolite. These chemical and morphological changes affected the ethylene scavenging activity of sepiolite. Therefore, the simultaneous modification of sepiolite by MW-assisted acid activation and ZnO assembly revealed to be a suitable approach for obtaining porous nanocomposite materials with higher specific surface areas than the commercially available, enhancing their potential for food packaging application.

### Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials (UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020) and CERENA research Unit (UIDB/04028/2020, UIDP/04028/2020), financed by national funds through the FCT/MEC (PIDDAC). FCT is also thanked for the Investigator FCT program (PF, IF/00300/2015) and Scientific Employment Stimulus program (IG, CEECIND/00430/2017). JS also thanks FCT for funding the SFRH/BD/145660/2019 grant. COST CA20126 is also acknowledged.

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## PEEK Nanostructures and Nanocomposites obtained by Hot Embossing into TiO<sub>2</sub> nanotube layers

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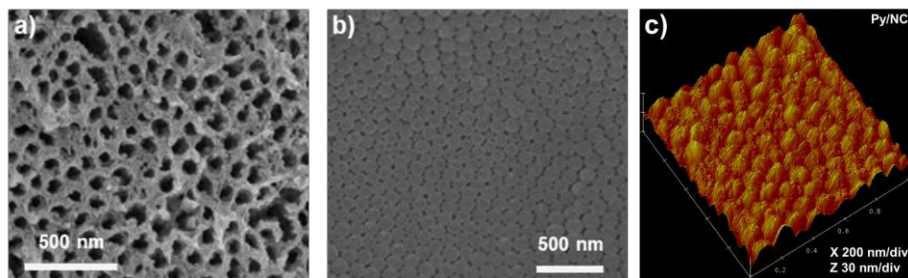
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Poly-ether-ether-ketone (PEEK) is a semicrystalline thermoplastic polymer with outstanding physical and chemical properties. PEEK is qualified for harsh conditions e.g. vacuum, cryogenic and radiation. The technological applications of PEEK extends from biomedical to aerospace fields. Moreover, PEEK is compatible with additive manufacturing processing. PEEK has been employed also as matrix for nanocomposites providing new capabilities for aerospace applications. In this work, we present the resulting PEEK nanostructured surfaces and composites, after fast and scalable hot embossing (nanoimprint) process[2] into anodic TiO<sub>2</sub> layers[3]. The resulting nanostructured surfaces morphologies are porous PEEK surfaces (Fig.1 a) and TiO<sub>2</sub> nanodomains in a PEEK matrix (Fig.1 b). The nanoporous surfaces withstand acid etchants and vacuum conditions, and are stable below 300 °C, which make them suitable for aggressive environments including some space and planetary conditions. On the other hand Magnetic Permalloy (Py) thin films have been deposited on TiO<sub>2</sub> nanodomains (Fig.1 c) showing interesting magnetic properties[4].

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### Figures



**Figure 1:** a) Nanoporous PEEK surface b) Nanodome surface c) AFM image of Py deposited on nanodomains



## Microwave-Assisted Flow Synthesis of Nano-confined Pt in Titania Nanotubes (Pt-TiNT) photocatalysts

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Pt-TiNT with PtO nanoparticles dispersed within the lumen and interlayer spaces of titania nanotubes (TiNT) were prepared by a new process involving titania nanosheets (TiNS) synthesis in an optimised microwave-assisted flow reactor, followed by ion-exchange with a Pt precursor, before triggering the titanate layer rolling to trap the Pt precursor clusters inside the titanium nanotubes, and thermal treatment. TEM, XRD and Raman analyses confirm the total conversion of TiO<sub>2</sub> into TiNS in 15 min at 120°C and 4 bar, and TiNS transformation into 181 nm-long TiNT with 10 and 6 nm outer and inner diameter, respectively. The 2% Pt-TiNT comprises PtO clusters (according to XPS) of 0.7 nm diameter, causing slight distortions of the interlayer spaces while some larger 2-3 nm Pt clusters reside within the lumen. Pt-TiNT is 14-fold more active than TiNT for visible light photocatalytic oxidation of diclofenac and more than 1000-fold better than the uncatalyzed photoconversion reaction. Nano-confinement of PtO clusters narrowed the bandgap of the TiNT, which combined with its excellent absorptivity to harvest light allowed a large spectral range of photon energies to activate the photocatalyst.

This work is supported by the Horizon 2020 BIORIMA project and the Hong Kong Research Grant Council E-HKUST601/17 and in part by the Project of Hetao Shenzhen-Hong Kong University of Science and Technology Innovation Cooperation Zone (HZQB-KCZYB-2020083). Dr. Y.J. Luo stay at the Instituto de Catálisis y Petroleoquímica is supported by the HKUST Overseas Research Award. Finally, the authors acknowledge the support of the Central Facilities of the Hong Kong University of Science and Technology including the Material Characterization and Preparation Facility (MCPF) and the Environmental Central Facility (ENVF).

## Graphene-based smart inks for electroanalysis.

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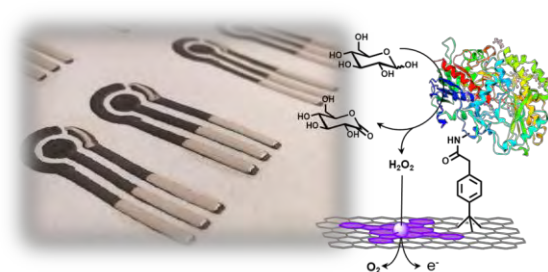
Originally discovered as a black pigment, carbon ink played an essential role in human civilization by helping to transmit and spread knowledge. The recent discovery of nano-structured carbon materials (e.g., fullerenes, carbon nanotubes and graphene) are enabling a new generation of programmable inks able to implement advanced functionalities far beyond color.[1] The coupling of these functional inks with modern printing technologies is revolutionizing the field of flexible electronics, and of wearable and implantable sensors and actuators.

This talk will elucidate different strategies, spacing from chemical functionalization to self-assembly and phase engineering, to achieve graphene and 2D material-based inks responsive to chemical concentrations. [2] In particular, our efforts have been focused in creating multifunctional inks able to fulfill all the requirements of an electrochemical sensor: immobilization and stabilization of the bioreceptors, recognition of the analyte, transduction, and amplification of the signal [2,3]. These smart inks were used to fully inkjet-print electrochemical paper analytic devices (e-PADS), obtaining low-cost, sustainable, and reliable platforms for electroanalysis.

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### Figures



**Figure 1:** Electrochemical paper-based analytic devices (e-PADS), fully inkjet-printed with graphene-based smart inks.

## Acousto-optofluidics for rapid laser-generation of periodic surface nanostructures

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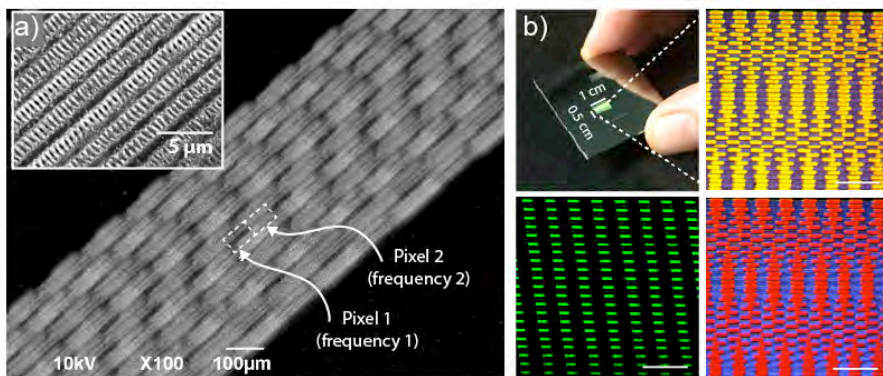
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### Abstract

Laser-induced periodic surface structures (LIPSS) offer remarkable opportunities for nano-optics and nanophotonics<sup>1</sup>. LIPSS are simple to prepare, indeed, they spontaneously form upon the irradiation of metals, semiconductors, or dielectrics with focused ultra-short laser pulses. Moreover, the selection of the laser parameters (e.g., fluence or polarization) allows nanostructuring a target surface with tailored optical properties. Nonetheless, synthesizing LIPSS over large areas is a slow process because of the inherent serial nature of any laser direct-write systems.

A method to solve this problem is exploiting light interference patterns that, irradiating a region rather than a point, enable large-scale processing of materials at sub-wavelength resolution. However, traditional tools for generating interference patterns lack tunability or operate at extremely low speed (temporal scale 10 ms) that impedes inter-pulse pattern selection at repetition rates of common lasers.

To overcome the above limitations, we present a method for the high-throughput generation of LIPSS in semiconductors and metals. Precisely, large-area ( $\sim\text{cm}^2$ ) nanopatterning is achieved with a novel light shaping tool that exploits the interaction between acoustic and light waves in a liquid to generate and select laser interference patterns at exceptional speed (temporal scale  $<1\ \mu\text{s}$ )<sup>1,2</sup>. Successful preparation of LIPSS and their on-the-fly (while scanning the sample surface) arrangement into user-selectable patterns is demonstrated by controlling amplitude, frequency, or phase of the acoustic waves (Fig. 1a). This strategy allowed stitching, on the same substrate, LIPSS-pixels with various structural colorations (Fig. 1b).



**Figure 1:** a) Scanning electron micrograph of a LIPSS pattern with two pixels obtained by snake scanning a palladium substrate with a femtosecond laser while the acoustic frequency swaps between 1.2 and 1.8 MHz. The inset shows LIPSS in the irradiated regions. b) Large area structural colors for different modulation rates of the acoustic frequency. Various structural colors appear by illuminating the pattern with white light at various angles of incidence. Scale bar 500  $\mu\text{m}$ .

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## Deposition of UV-filter oxide films on cork and rubber – protection to UV radiation and from mechanical wear

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**Abstract:** The sun's ultraviolet rays strongly contribute to the aging and discoloration of some outdoor products. In addition, they may suffer severe mechanical wear when subjected to friction. This is especially critical for materials like cork and rubber, natural materials with distinctive specific properties such as high elasticity, high porosity and thermal and acoustic insulation. Both products have a wide range of applications ranging from wine stoppers and gym flooring to footwear and aerospace industries. Solving these issues while keeping their original properties is a challenge of this work. Deposition of metallic oxide thin films with high transmission in the visible region and high absorption in the UV range, but also resistance to mechanical wear, may be the adequate solution to solve the referred problems. TiO<sub>2</sub> and ZnO thin films are potential candidates. Cork and rubber are difficult to coat since they are granulated, have high deformation and roughness, and are temperature sensitive. Despite these challenges, TiO<sub>2</sub> and ZnO thin films were successfully deposited by magnetron sputtering (MS) and atomic layer deposition (ALD) on both products. The deposited TiO<sub>2</sub> thin films show high transmission in the visible range and they block radiation with  $\lambda < 320$  nm, but ZnO thin films reveal better behavior since they can block radiation with  $\lambda < 380$  nm. Sun exposure tests proved the best protecting performance of the ZnO films. Mechanical properties such as tensile tests, scratch tests and hardness were investigated for both coated and uncoated materials as well.

## Conversion of CO<sub>2</sub> to High Added Value Nanocarbons

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### Abstract

Nowadays, decrease of carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere through carbon capture and conversion processes, is a key player in reducing climate change issues since it can positively impact the total levels of greenhouse gases<sup>1</sup>. At the same time, preparation of advanced nanocarbons like graphene, CNTs, CNFs, and their composites through effective environmentally benign procedures remains in the focus of intensive research<sup>2, 3</sup>. In the present work, a simple scalable method for conversion of the greenhouse gas CO<sub>2</sub>, to high added value nanocarbons with controlled morphology is described. Molten salt electrochemical systems consisting of eutectic mixtures of alkaline carbonates (Li, Li-K, Li-K-Na) as electrolytes, Ni-Cu or galvanized iron (Fe) electrode as cathode and, Ni-Cr electrode as anode, were applied for the conversion of CO<sub>2</sub> to nanocarbons using electrolysis. During molten-salt electrolysis, CO<sub>2</sub> was flow through the electrolyte, and carbons with various morphologies were deposited on the cathode. The produced nanocarbons were washed with HCl, dried at vacuum oven and activated under CO<sub>2</sub> gas flow at high temperature. The structure and the morphology of the prepared materials were examined employing X-ray diffraction analysis, scanning electron microscopy, nitrogen porosimetry and electrochemical characterization.

It was demonstrated that tuning the nanocarbons morphology can be achieved by regulating the electrolyte composition and electrolysis parameters. In pure Li<sub>2</sub>CO<sub>3</sub> electrolyte, carbon nanofibers (CNFs) were synthesized at 790°C. Nanocarbons with different morphologies (lamellar, vertical oriented, sheet-like) were obtained in Li-K at 600–650°C. Amorphous carbon with irregular shaped morphology obtained in Li-Na-K at 600°C, while honeycomb carbon generated in Li-Na-K at 500°C.

Activated carbon exhibited outstanding electrochemical performance ascribed to its high specific surface area (1020 m<sup>2</sup>/g) compared with non-activated one. The porosity and the cyclic voltammetry, charge-discharge and impedance measurements evidenced that the prepared nanocarbons can be used for energy storage, while the suggested environmentally benign preparation method can be scaled up to industrial extent due to simplicity.

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### Acknowledgments

The authors appreciate the financial support from the project "T1EDK-01729 CARBONGREEN" (MIS 5048538) co-financed by the European Union and Greek National Funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE.

## Copper-functionalized organic semiconductor for electrocatalytic CO<sub>2</sub> reduction

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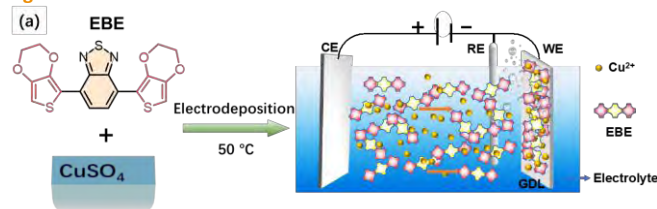
### Abstract

Organic Semiconductors are attracting increasing attention owing to their delocalized conjugated system and outstanding electrochemical property, electrical conductivity, and high carrier mobility.<sup>1</sup> In particular, the semiconductor redox potentials of CPs can be precisely modified through design of molecular structure such as donor-acceptor junctions. Recently, conjugated polymers have been studied as (photo)electrocatalysts for HER, OER. However, the performance of CPs for CO<sub>2</sub> reduction has been rarely investigated due to the complexity of the reaction that undergoes multi-electron and multi-proton pathways. Herein, we synthesize a copper-functionalized conjugated trimer with donor-acceptor-donor molecular structures by electrodeposition. With the synergistic effect between Cu and conjugated trimer, the composites can selectively reduce CO<sub>2</sub> to ethylene with a high Faradaic efficiency (max. 55% at -1.6 V) in broad potential windows and large current density (60 mA cm<sup>-2</sup>). It is thus desirable to develop a family of heterogeneous catalyst with molecularly regulating electrocatalytic activity. The variation of activity in small molecules are strongly correlating with their physical properties such as energy band levels, and lifetime of excited particles. The results indicate that conjugated small molecules are promising applications in electrocatalytic chemical energy conversion.

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### Figures



**Figure 1:** Experimental process for synthesis of Cu-EBE by electrodeposition.

## Optimization of the composite cathode for Li-sulfur batteries

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### Abstract

Li-sulfur batteries represent a promising energy storage system due to their large theoretical capacity (1675 mAh/g), safety, and nontoxicity. Despite the long-term effort, fundamental issues remain to be solved before their commercialization. Along with the non-conductivity of elemental S and large volume changes during redox reactions, the main problems are related to the initial formation of highly soluble lithium polysulfides (PS). The cathode architecture represents a scientific challenge. It must contain an electronically conductive additive with special morphology permitting the electrochemical reduction of non-conductive sulfur and buffering volume changes during its reduction to soluble higher polysulfides (PS) and their oxidation back to elemental sulfur. Conductive carbonaceous materials with various morphology have been demonstrated to enhance the performance of sulfur-based cathode composites. Further improvement of this system represents using an additional inorganic component for the efficient immobilization of PS. As the inorganic additives can be used transition metal oxides[1-3], suboxides[4], nitrides[5] or sulfides[6].

In our presentation, we demonstrate the effect of the TiO<sub>2</sub> top layer prepared by our facile fabrication protocol on the charge capacity of the sulfur/composite cathode in the Li-sulfur battery. The TiO<sub>2</sub> top layer on the cathode increases its charge capacity by 40-60% as compared to the cathodes with titania-free materials.

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## Influence of nanoporous anodic alumina barrier layer thinning on electropulsed deposition Ni nanorods for energy storage applications

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### Abstract

In the present climatic emergence situation, the reduction of unsustainable resources stimulates great research efforts on renewable energy. One of the key technologies is energy storage where supercapacitors (SCs) provide a means to store energy with quick charge/discharge rates and large cycle number. To improve SCs performance, nanostructuring of the electrodes offers a larger surface area for charges to store [1]. Nanoporous anodic alumina (NAA) can be used as a template for the preparation of nanostructured electrodes by the application of electrodeposition of metals within the pores [2]. This is only possible when a metallic contact at the bottom of the pore is provided so that metallic ions in solution can be reduced and deposited. Such metallic contact is achieved following the procedure in ref. [3] where a final etching step to remove the residual barrier layer is crucial to provide uniform contact through all the sample.

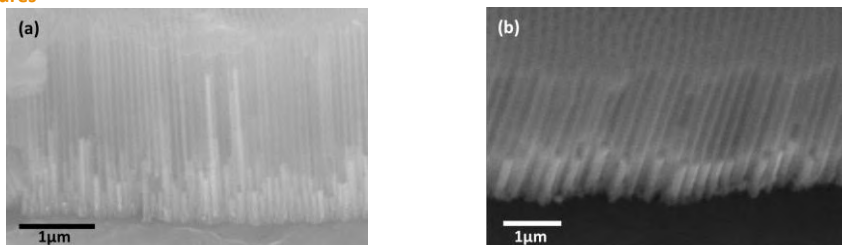
In this work, we study the influence of the time extent of this final etching step ( $t_E$ ) on the uniformity and morphology of deposited Ni nanorods. NAA templates were synthesized with the two-step anodization procedure followed by a third step reanodization for in-situ thinning of the barrier layer. Subsequently, the final etching step with 5 wt% phosphoric acid solution at 35 °C is applied for a time extent  $t_E$ .

Fig. 1 shows deposited Ni nanorods for two samples with different final etching times. Fig. 1(a) corresponds to the  $t_E=10$  min. while Fig. 1(b) corresponds to  $t_E=15$  min. For the shorter etching time a large dispersion of the Ni nanorods length, with values ranging between 200 nm and 1  $\mu\text{m}$ , can be observed. Instead, the longer etching time shows a more uniform distribution of lengths around 250 nm. Shorter etching times lead to an even bigger length dispersion because of an incomplete barrier layer thinning. On the other hand, longer pore widening times result in an excessive dissolution of the pore walls. From these results we can conclude that the optimum time for the final etching is about 15 minutes as it gives homogenous contact throughout the sample for Ni deposition. These obtained metallic nickel nanorods by electropulsed deposition can be used as electrodes for the application of high-performance SCs.

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### Figures



**Figure 1:** Ni nanopillars obtained by pulsed electrodeposition in NAA. a) nanopillars obtained for barrier-layer etching time  $t_E = 10$  min. b) nanopillars obtained for  $t_E = 15$  min.



## Development of electrospun nanofibers membranes with magnetic properties

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Electrospinning is a technique suitable for obtaining polymeric fibers with diameters in the nanometer and micrometer range from a polymeric solution thanks to the electrostatic force created between two electrodes, i.e. the tip of the capillary syringe, where the drop of the polymeric solution is formed, and the grounded collector, where the fiber membrane is deposited [1]. Thus, it can be considered as a versatile technique for high porosity and high surface-to-volume ratio membranes production, which can be used in a wide range of applications such as nanocatalyst, protective coatings, membranes, filtration and wound dressing, among others [2].

On the other hand, magnetic properties of magnetic nanomaterials make them good candidates for being used in different research areas and multidisciplinary studies. Among them, magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ ) are the most widely studied one due to their properties. The incorporation of these nanoparticles into polymeric structures, allows the obtaining of lightweight, flexible and magnetic polymeric nanofiber membranes, which are known to be very promising materials in numerous application fields.

In this study,  $\text{Fe}_3\text{O}_4$  nanoparticles prepared by the co-precipitation method from an aqueous  $\text{Fe}^{3+}/\text{Fe}^{2+}$  solution (3:2 molar ratio) using ammonium hydroxide in excess, were coated with oleic acid, and used to provide magnetic properties to electrospun polyurethane nanofiber membranes (Figure 1). The content of  $\text{Fe}_3\text{O}_4$  nanoparticles was varied to modulate the magnetic properties of the membranes.

Financial support from MICINN/EU/FEDER/AEI (PID2019-105090RB-I00 / AEI / 10.13039/501100011033), from GV/EJ (Grupos Consolidados IT-1690-22) and from EUROREGION Nueva Aquitania-Euskadi-Navarra (RECYCLEPOLYWASTE) is gratefully acknowledged.

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### Figures



Figure 1: Sequence of digital images of the magnetic response of an electrospun membrane with  $\text{Fe}_3\text{O}_4$  nanoparticles.

## Electrospun Membrane of Thiolated Polyurethane Nanofibers

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Polymeric nanofiber membranes incorporating versatile functionalities are known to be very promising materials in numerous application fields. Segmented polyurethanes (PU) are block copolymers with enormous flexibility in their chemical structure, processing technologies and final properties, and are therefore considered ideal candidates for the development of functional nanofibers [1]. The incorporation of specific chemical moieties into the PU backbone is highly desirable when ulterior physical interactions or chemical reactions are required. In this context, the synthesis of taylor-made PUs is proposed by inserting pendant clickable groups along the main chain, suitable for subsequent click reactions with molecules or polymers suitably functionalized with the conjugate, after the electrospinning process.

In this study, two biocompatible biobased PU formulations containing thiol (PU-SH) and maleimide (PU-Mal) pendant groups were synthesized and processed by electrospinning. On the one hand, nanofibers containing thiol moieties were electrospun to obtain membranes. The thiol-maleimide click reaction was verified with a fluorescently labeled maleimide model molecule adjusting the pH to 5.5 (Figure 1 Left). On the other hand, PU-SH and PU-Mal were processed simultaneously by coaxial-electrospinning for the preparation of nanofibers containing thiol and maleimide groups in stoichiometric ratio. Triethylamine and UV light were used to promote the thiol-michael reaction. The nanofiber membranes were mechanically characterized before and after click reaction, observing an increase in the strength, stiffness and elongation of the clicked membranes (Figure 1 Right).

Financial support from MICINN/EU/FEDER/AEI (PID2019-105090RB-I00 / AEI / 10.13039/501100011033) and from the GV/EJ (Grupos Consolidados IT-1690-22) is gratefully acknowledged.

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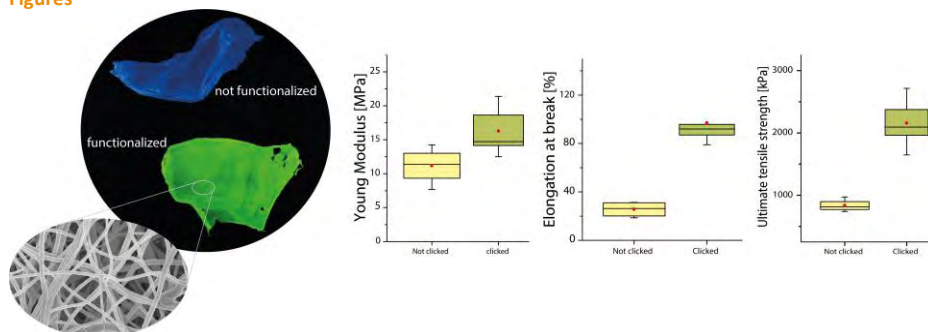


Figure 1: Left: functionalized and not functionalized membranes. Right: Mechanical properties of clicked and not clicked membranes.

## Photoluminescence sensor based on nanoporous anodic alumina for Endoglin 105 detection

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Nanoporous anodic alumina (NAA) is a porous material obtained through the oxidation of aluminium. This oxidation is done by an electrochemical process based on an acid solution. Depending on the used acid, different pore sizes are obtained from 18 to 120 nm approximately [1]. The possibility to control the different parameters of the anodization (temperature, potential and charge), allow us to fabricate NAA with different morphologies such as bilayers that can be used to detect more than one [2]. This also let us adjust the optical properties of NAA, making it interesting for many sensing, drug delivery and tissue engineering applications [3]. One of its interesting properties is the photoluminescence (PL) [4], which is an optical property in which the material gets excited to a higher energy state due to the absorption of light and emits a photon on the return of its electron back to a lower energy state. In this work, we study the effect on the photoluminescence of NAA infiltrating gold nanoclusters on its structure following by the, the gold nanoclusters functionalization with a specific antibody, for the detection of different concentrations of Endoglin 105. Figure 1a shows the FESEM cross section of NAA structure. Figure 1b shows the changes on the PL while adding different concentrations of Endoglin 105. The results showed the photoluminescence response at 425 nm, corresponding to the NAA, and it also showed a peak at 600 nm, corresponding to the gold nanoclusters when binned to the NAA surface.

**Acknowledgments:** This work was supported by the Spanish Ministerio de Ciencia e Innovación (MICINN/FEDER) PDI2021-128342OB-I00, by the Agency for Management of University and Research Grants (AGAUR) ref. 2021-SGR-00739, by the Diputació de Tarragona (DIPTA) 2022/33, Juan de la Cierva incorporation fellowship (IJC-2019-042374-1), Beatriz de Pinos Grant (2021 BP 00105) and by the Catalan Institution for Research and Advanced Studies (ICREA) under the ICREA Academia Award

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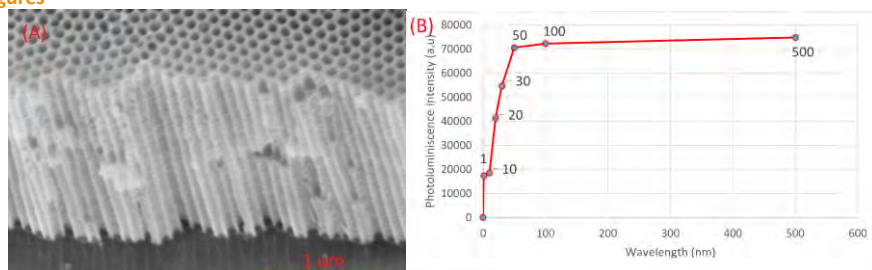


Figure 1. (a) FESEM images of NAA cross-section structure. (b). PL response of different concentrations of Endoglin 105 incubated in NAA-functionalized with gold nanoclusters.

## Towards Chiral Acoustoplasmonics

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### Abstract (Calibri

8The possibility of creating and manipulating nanostructured materials encouraged the exploration of new strategies to control electromagnetic properties. Among the most intriguing nanostructures are those that respond differently to helical polarization, i.e., exhibit chirality.[1] Circularly polarized light can be used to probe and determine the chiral nature of a plasmonic structure, which is usually reflected as quantitative differences in the values of the absorption or scattering cross-sections. However, reaching maximum absorption and minimum scattering for one helicity, and the opposite for the other is not usually found to occur at the same wavelength [2].

In the present work, we propose a simple chiral plasmonic structure based on crossed elongated bars where light-handedness defines the dominating cross-section absorption or scattering, as it identifies the two different enantiomers in a chiral structure which determine how the system interacts with its environment. The system is yet maintained simple enough to understand the actual nature of the response observed, be open to future developments, and warrant fabrication for future experimental verification [3]. Based on this structure, our work demonstrate that, not only through the interactions between different elements it is possible to make the absorption and scattering cross-sections radically and qualitatively different for the two circular polarizations, but the dominating cross-section can be switched from absorption to scattering by simply changing the polarization of the impinging beam [4]. Also, we theoretically propose a simple pump-probe experiment using circularly polarized light. In the reported structures, the generation of acoustic phonons is optimized by maximizing the absorption, while the detection is enhanced at the same wavelength -and different helicity- by engineering the scattering properties [5]. The presented results constitute one of the first steps towards harvesting chirality effects in the design and optimization of efficient and versatile acoustoplasmonic transducers.)

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## Engineering of Au-Al nanopatterned substrates as platforms for SERS detection.

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From its early 1974 description, surface-enhanced Raman scattering (SERS) has attracted considerable attention due to its potential utility in a wide variety of fields throughout the life sciences, including analytical chemistry, biomedicine, agriculture, and more. To create SERS-based ultrasensitive sensors of diverse substances, highly branched metal nanostructures are of great interest [1].

Our results provide a robust strategy for assembling Au nanoparticles (NP) into Al high-density nanoarrays with high spatial resolution, providing intense electromagnetic fields for plasmonic sensor applications. With the help of a two-step anodization technique [2], we were able to replicate the unique honeycomb structure and its ability to build Au nanoparticle patterns on arrays of honeycomb-like Al nano bowls.

The initial anodization step of a two-step anodization process consisted of the application of 40 V to Al sheets in an oxalic acid electrolyte at 5 °C for 20 hours. The pattern formed on the Al template during this initial anodization was removed by immersing the samples in an etching solution of 1.8% chromic acid and 6% phosphoric acid (etching solution) for 3 hours at 70 °C. Then a second anodization step for three further hours was done under the same initial step parameters [2]. Finally, the samples were treated with the same previously used etching solution for 2 hours at 70 degrees Celsius to remove the formed nanoporous alumina, as shown in Fig 1. A thin coating of gold was deposited on the prepared Al nano bowl substrates using RF magnetron sputtering (BESTEC, magnetron sputtering system). Thereafter, the nano bowl substrates with the Au films were annealed at various temperatures and time intervals.

The Au film sputtering time and the annealing conditions affected the AuNP size and distribution. These electrochemically produced nanoarrays provide high spatial resolution due to dense Au NPs. Their plasmonic characteristics, experimentally measured from the visible to the NIR region, with significant Enhancement Factors for molecule detection, make them excellent substrates for sensitive applications like SERS [3]. This work will enable rapid identification and classification of target analytes in clinical applications, food safety, environmental pollution, chemical hazards, and label-free detection of DNA, proteins, viruses, cells, and other biological systems.

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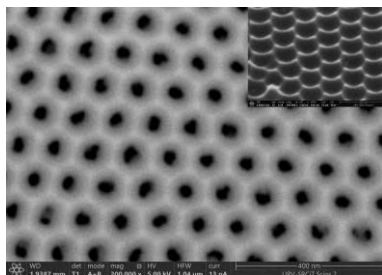


Figure 1: Porous morphology of the alumina layer. Inset: Al nanoconcavities.

## 2D WSe<sub>2</sub>: synthesis and characterization

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### Abstract

Since the first isolation of graphene in 2004 the interest in 2D materials has exponentially grown. Two-dimensional layered materials demonstrate profoundly different properties when isolated in their mono- or few layer form compared to their bulk equivalents. An important class of layered materials is the transition metal dichalcogenides (TMDs). These materials has generated a lot of attention due to their electronic properties, which range from metallic to semiconducting, as well as their layer-dependent properties and strong light-matter interactions. TMDs consists of a transition metal e. g. Mo, W or Pt, sandwiched between two chalcogen atoms; S, Se or Te.

WSe<sub>2</sub> is a semiconducting material in both bulk and monolayer form. Bulk WSe<sub>2</sub> has an indirect band gap of 1.2 eV which transitions to a direct band gap of 1.65 eV in the monolayer material [1]. The material differs from other TMDs as it has relatively smaller effective electron and hole masses and is ambipolar [2]. Due to the ambipolar properties of WSe<sub>2</sub>, the material can be used as both a n-type or a p-type charge carrier material, depending on the contact material [3]. 2D WSe<sub>2</sub> were synthesized by TAC method. In thermally assisted conversion (TAC), a layer of transition metal is deposited on the surface by sputtering or evaporation. The metal layer is subsequently converted to a TMD by heating it in a furnace under a chalcogen-containing vapour flow. The TAC process can result in the production of large-scale polycrystalline TMD that has a few- to multilayer thickness with grain sizes in the order of 10-100 nm. The obtained nanolayers are studied by AFM, Raman spectroscopy, optical microscopy and TEM.

Acknowledgement: We are grateful for the financial support from Bulgarian Science Fund project number KP-06-H-28/8. V. M. and P. R. acknowledge the financial support by the European Regional Development Fund within the Operational Programme 'Science and Education for Smart Growth 2014–2020' under the Project CoE 'National Center of Mechatronics and Clean Technologies' BG05M2OP001-1.001-0008-C01

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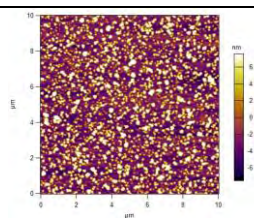


Fig.1 AFM of WSe<sub>2</sub> (5s precursor)

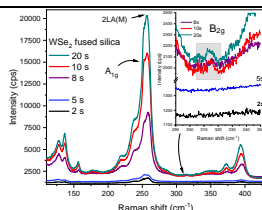


Fig.2 Raman spectra of WSe<sub>2</sub> with different thickness

## THEORETICAL STUDY OF BIMETALLIC PLASMONIC NANOSTARS AND THEIR EFFICIENCY AS PHOTOCATALYSTS

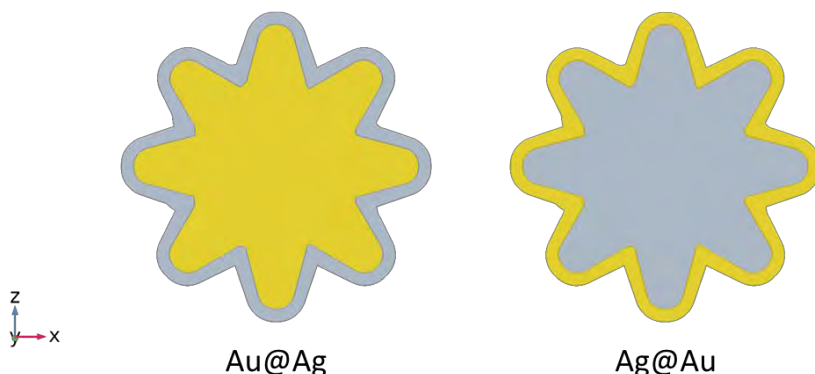
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Nanostars (NSs) provide a very promising template for the study of plasmonic-enhanced processes, in particular driving photocatalytic reactions, due to their intense hot-spots, which are combined with a quasi-spherical symmetry that separates them from plasmonic nanorods [1]. It is still an open question, however, how to best exploit these nanostructures in different specific applications, as their response is very sensitive to small changes in their properties, and using this geometry in multimetallic systems, which have shown great promise in the past,[2] further expands the space of possibilities.

We present a work in which we have precisely explored how multimetallic NSs respond in a photocatalytic context. We have performed a computational study of the optical response of different NSs made of gold and silver, modelling bimetallic NSs grown experimentally. Our theoretical approach allows us to study the expected relative importance of different energy transfer mechanisms between plasmonic NS and environment to the photocatalytic process. With these results, we can critically evaluate the expected photocatalytic outcomes of using silver-coated and uncoated gold NSs. We also studied the reverse system, gold-coated silver NSs, with the same geometries, to offer a comprehensive discussion of the use of multimetallic systems in photocatalytic applications.

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**Figure 1:** Schematic representation of a transverse cut at the center of the nanostars studied in this work. Left: Au-core@Ag-shell nanostar. Right: Ag-core@Au-shell nanostar.



## Tuning the composition of multidoped magnetite nanoparticles starting from bimetallic FeMn, FeCo and FeZn oleates

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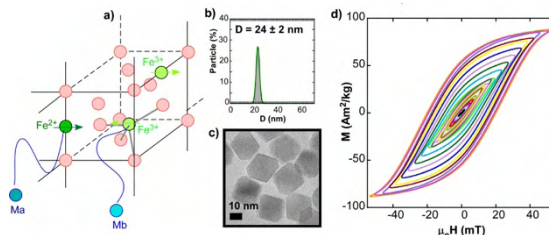
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The preparation of nanostructures with specific sets of features (composition, size and morphology) requires a fine control over the synthetic protocol<sup>1</sup>. Specifically, iron oxide nanoparticles (IONPs) have become versatile building blocks for a wide range of biomedical applications including magnetic hyperthermia, magnetic resonance imaging and drug delivery among others. In this sense, the thermal decomposition of organometallic precursors allows synthesizing novel iron oxide-based magnetic NPs (MNP) with a well-defined size and morphology<sup>2</sup>. The introduction of a low quantity of divalent transition-metal ions ( $M_xFe_{3-x}O_4$ ,  $M = Mn, Co$  and  $Zn$ ) within the spinel structure of MNPs has proven to be a good strategy to obtain mixed ferrites with tuned magnetic performance. Herein, we present an improved chemical route to synthesize Mn/Co/Zn-doped magnetite NPs based on the thermolysis of bimetallic oleates ( $Fe_{3-n}M_nOl_{9-n}$ ). Following a similar approach, two types of M-doped magnetite NPs have been synthesized: *i*) Single-doped magnetite NPs ( $M_xFe_{3-x}O_4$ ) and *ii*) Multi-doped magnetite NPs ( $Ma_xMb_yFe_{3-x-y}O_4$ ) with a metal content of  $0.02 < x, y < 0.2$ . This synthetic protocol has led to a set of highly homogenous cuboctahedral NPs with average sizes ranging from 16 to 32 nm, with large saturation magnetization values ( $\geq 86 \text{ Am}^2/\text{kg}$  at RT). These samples have been chemically, structurally, morphologically and magnetically analyzed making use of Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and DC Magnetometry. Finally, the biomedical potential of the whole set of samples in the magnetic hyperthermia therapeutic modality has been analyzed in detailed by measuring the dynamical hysteresis loops at different frequencies (up to a field intensity of 90 mT). Some of the samples have shown a great magnetothermal efficiency ( $> 600 \text{ W/g}$ ) under clinical safety limits (36 kA/m and 125 kHz), with makes these nanoparticles promising candidates for future magnetically-mediated medical devices.

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### Figures



**Figure 1.** a) Asymmetric unit of  $Fe_3O_4$  lattice, b, c) TEM image, corresponding size distribution and d) AC hysteresis loops of a  $M_xFe_{3-x}O_4$  NPs sample.



## TiO<sub>2</sub> nanoparticles by electrospray

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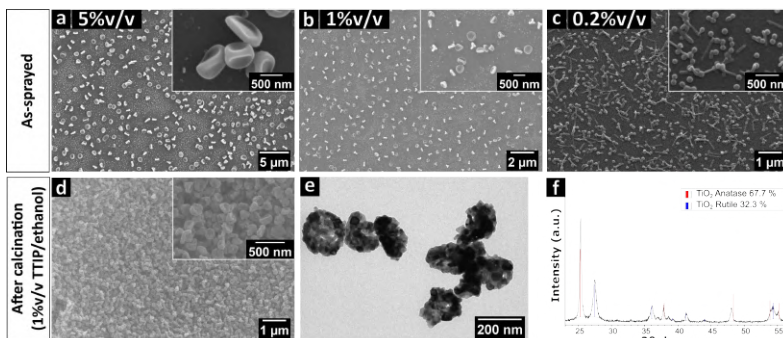
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Titanium oxide (TiO<sub>2</sub>) nanoparticles are known for their photocatalytic activity [1], among other applications. Dye-sensitized solar cells printed by electrospray often have superior performance to cells prepared by conventional methods, such as doctor blading and screen-printing [2]. In electrospray, a liquid containing either TiO<sub>2</sub> nanoparticles or an organometallic precursor (e.g., titanium (IV) isopropoxide (TTIP)) is atomized in a strong electrical field, by becoming a Taylor cone meniscus which ejects a stationary microjet. The jet breaks up into electrically charged droplets, which are electrophoretically deposited onto a conductive substrate [3,4,5]. Different TiO<sub>2</sub> particle morphologies have been reported [6]; however, the factors and mechanisms which determine those morphologies are not fully understood. In this work, we are mapping out the process parameter space to quantify the morphology dependence on the operational parameters, with the aim to improve the performance of the TiO<sub>2</sub> nanoparticles. We produce TiO<sub>2</sub> nanoparticles by calcining the dry residues of electrosprays of solutions containing organometallic precursors. Several concentrations of TTIP/ethanol were used. Although water is probably responsible for the precipitation of the titanium (as hydroxide), moisture in the electrospray ambient was found to be disadvantageous to the stability of the Taylor cone. We produced TiO<sub>2</sub> nanoparticles, obtaining a 70/30 anatase-rutile ratio and a size of 20-40 nm.

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### Figures



**Figure 1:** Electrosprayed nanoparticles at different solute concentrations in the TTIP/ethanol solution: (a,b,c) as-sprayed. For 1%v/v calcined (650°C): (d) SEM and (e) TEM images, and (f) XRD spectra.

### Acknowledgements

The Spanish Government and the EU (grant PID2021-129064NB-I00), the FPU scholarship programme (grant FPU19/03733), and Catalan Government (grant 2021SGR-00978).

## SILICONE COMPOSITES WITH RGO AND NANOSIZED ZINC OXIDE

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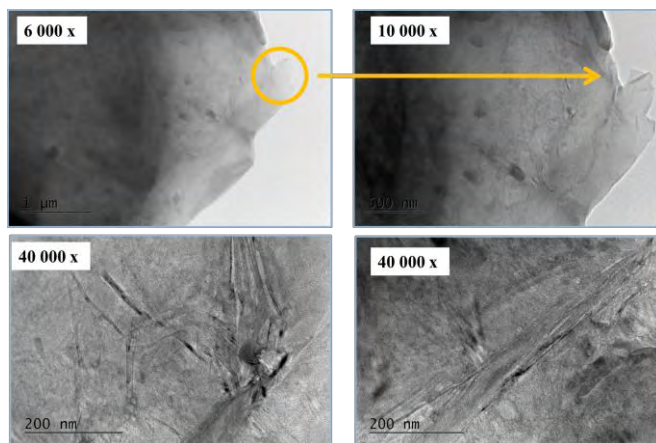
The development of advanced silicone composites involving graphene materials is an attractive area of research due to graphene's potential to improve the mechanical and functional properties of silicone. New formulations of silicone composites in the form of coatings on glass substrates were obtained with the participation of GO, RGO and ZnO additives. All newly obtained composites were investigated by XRD, SEM and TEM analysis. The presence of silicone rubber in all samples, as well as RGO and ZnO, was demonstrated by means of X-ray diffraction. Using the computer program QualX, the size of ZnO NPs in the composites was determined. By SEM, agglomerates of ZnO and RGO distributed over the compact silicon structure were observed. The microstructure of the well-separated carbon layers of RGO and elongated ZnO nanocrystals embedded in the silicon matrix was observed by TEM. From the selected area electron diffraction (SAED) study of a silicon composite with 5 % ZnO and 5 % ZnO/(5 %) RGO, a conclusion was made about the structure of the ZnO nanocrystallites and the type and parameters of the crystal lattice were determined. Using the agar diffusion method, the antibacterial activity of the obtained composites was determined against the bacteria *Escherichia coli* and *Staphylococcus aureus*.

**Acknowledgments:** Authors acknowledge the financial support of the National Science Fund of Bulgaria, Project KP-06-H27/17 17.12.2018

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### Figure



**Figure 1:** TEM images of silicone composite with 5 % RGO at different magnifications.

## A Nanotechnology approach to enhance the sweetness profile in low-sugar foods

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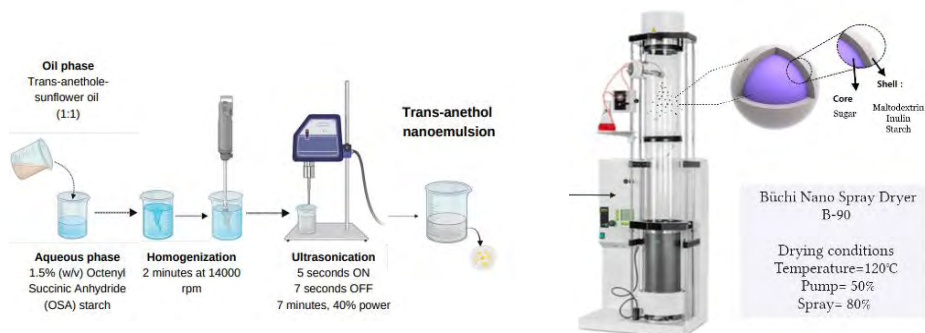
### Abstract

Sugar consumption has become a major contributing factor to many common health diseases affecting the population. In response, the food industry has been taking steps to reduce sugar content and develop sugar alternatives with lower calorie intake. However, it's important to note that the substitution and reduction of sugar may lead to decreased consumer acceptance of certain food products. Nonetheless, with the potential to enhance food quality, extend shelf life, develop intelligent packaging, and create new ingredients with a higher sweetening capacity, nanotechnology presents an opportunity to revolutionize the food industry. Nanoencapsulation can also be used to develop food additives that can enhance the nutritional value of food products [1]. Furthermore, nanotechnology can help improve the sensory properties of food products such as flavour, texture and appearance. For example, nanoparticles can be used to create emulsions that improve the texture of food products, or to encapsulate flavours and fragrances that can be released when the food is consumed.

This project aimed to evaluate the use of nanotechnology to produce new ingredients for food formulations. In this way, two approaches were tested to develop a novel method to reduce the sugar content in cookie formulations: nanospray dryer (NSD) and nanoemulsions (NE). The first approach involved reducing the particle size of sucrose to increase sweet mouth sensation, while the second approach was used to encapsulate trans-anethol, an essential oil with sweetening properties, in nanoemulsions produced by ultrasounds using modified starch as the emulsifier. After producing the nanoemulsion was produced also NSD was used for drying. From the first strategy, we obtained a powder composed of particles with size average of  $2.13 \pm 0.67 \mu\text{m}$  ( $n=400$ ). In the second strategy, the nanoemulsion showed particle sizes below 300 nm and PDI below 0.3 that after the NSD resulted in a powder of particles presenting a size average of  $2.07 \pm 0.59 \mu\text{m}$ .

To validate the sweetening capacity of the proposed strategies, obtained powders were incorporated into a cookie formulation with a 10% of sugar reduction and later compared to the commercial cookie brand as a control sample. A Temporal Check-All-That-Apply (TCATA) analysis with a semi-trained panel showed that the proposed formulations had a similar sweet profile compared to the control sample. However, the tests showed that formulations developed with trans-anethole nanoemulsions had undesired flavours that could be improved reformulating of the recipe. Overall, the study suggests that stabilising sweetener alternatives and restructuring sucrose using nanotechnologies are effective strategies for reducing sugar in food formulations.

## Figures



**Figure 1.** Nanotechnologies applied to food ingredients: (A) Stabilization of essential oil using nanoemulsions. (B) Microsized sugar obtained by nanospray-drying

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## Eu<sup>3+</sup>-doped NaBi(MoO<sub>4</sub>)<sub>2</sub> nanoparticles as contrast agents for bioimaging

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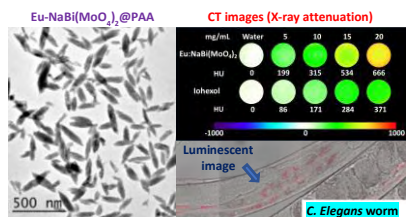
### Abstract

Lanthanide doped nanoparticles (oxides, fluorides, molybdates, etc.) have been widely investigated as probes for luminescent bioimaging [1]. On the other hand, the high atomic number (Z) of Bi (83) confers to the Bi compounds a strong capacity for X-ray attenuation and therefore could be used as probes for X-ray computed tomography (CT) [1]. Therefore, Eu and Bi containing nanoparticles could find applications as dual-mode probes for both, luminescent imaging and CT. In this work, we reported for the first time in the literature, a one-pot method for the synthesis and functionalization with polyacrylic acid (PAA) of uniform Eu<sup>3+</sup>-doped NaBi(MoO<sub>4</sub>)<sub>2</sub> nanoparticles [2]. The luminescent properties of such nanoparticles are evaluated as a function of the Eu<sup>3+</sup> doping level finding, in all cases, an intense red emission. The X-ray attenuation properties of the nanoparticles have been also analyzed, which showed better X-ray attenuation properties than iohexol (commercial computed tomography contrast agent). These nanoparticles could be well dispersed in water and 2-(N-morpholino)ethanesulfonic acid monohydrate medium (physiological pH simulator). Finally, the cell viability and *in vivo* toxicity using *C. Elegans* as a model of such phosphor have been evaluated, finding no significant toxicity up to a NPs concentration of 100 µg·mL<sup>-1</sup> (within the range required for most *in vivo* applications) being, therefore, excellent candidates for their use as bimodal probes for CT and luminescent imaging, the later being illustrated using the *C. Elegans* model.

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### Figures



**Figure 1:** TEM image of the nanoparticles, X-ray attenuation phantom images and X-ray attenuation values vs. contrast agent concentration compared with iohexol (commercial contrast agent) and localization of the nanoparticles (in red) through the intestine of the worm.

## Blood-brain barrier on a chip with integrated monitoring system

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In recent years, the use of microphysiological systems, capable of reproducing the essential functions of organs in our body *in vitro* has spread. These biomimetic systems are called organ-on-a-chip (OoC) for their ability to reliably reproduce the physiological environment. OoC model in combination with continuous monitoring systems, such as multi-parametric sensors has several advantages over the traditionally used tests.

The study of the physiology of the blood-brain barrier (BBB) arouses special interest, since it is one of the most extensive and selective semi-permeable barriers of the central nervous system, which acts as a natural barrier that protects the brain from the entry of neurotoxic agents, and the invasion of pathogens and circulating blood cells.<sup>1-2</sup> It is therefore a barrier difficult to cross for vascular medicines that are directed to the brain. Moreover, the permeability of this barrier is directly affected in many neurodegenerative disorders (NDDs), which makes this platform an excellent tool for its study. But to have a complete picture of the disease and an appropriate environment for the BBB, neurons must be also included into the system.

BBB-oC models in the published articles do not reach physiological permeability values and are poorly reproducible. Most of the reported works monitor the evolution of BBB formation using immunolabeling and microscopy. Still only few examples describe integrated techniques inside the chip, such as biosensors, which are often applied in medical diagnostics and other areas. The use of biosensors can bring many advantages to BBB-oC in achieving automated monitoring of a wide range of analytes and biomarkers for personalized disease study or drug testing in NDDs.<sup>3</sup>

The goal of our project is to design models of BBB-oC that reproduce the physiology of the barriers including 3D co-culture of neurons with an exhaustive control of the permeability and inclusion of biosensors for monitoring in a reliable way.

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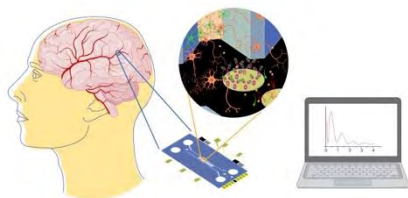


Figure 1: Schematic presentation of BBB-oC.

## Nanosized hydrogel dots for biomarker detection

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Hydrogels are interesting materials for biosensing applications. Their tridimensional nature and high water content make them an appropriate matrix for protein immobilization, while their inertness minimizes non-specific protein binding<sup>1</sup>. Hydrogels also offer the possibility to produce protein microarrays on non-functionalized substrates, in a cost-efficient way<sup>2</sup>.

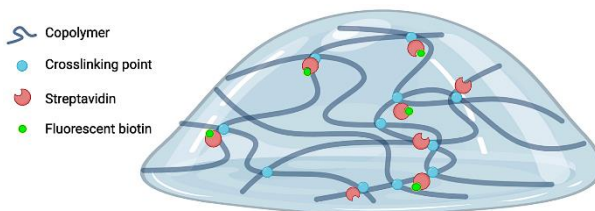
Here in this study we present a model for a biomarker sensor based on spotted picoliter-volume hydrogel drops with a thickness of few nanometers. The polymer contains photoreactive moieties, allowing for UV crosslinking after deposition of the dots on the substrate. In the same reaction, the polymer network was crosslinked and adhered to the substrate. When streptavidin was mixed with the polymer, the protein was immobilized in the matrix upon UV-crosslinking. In the first stages, the optimal crosslinking parameters were studied, and dot morphology was characterized with AFM and SEM.

For the proof of concept of the biosensing application, the streptavidin-biotin interaction was used to model an antibody-antigen interaction, and fluorescence was used for protein detection. In a first approach, the immobilization of streptavidin in the hydrogel matrix was studied using fluorochrome-tagged streptavidin. Then, regular streptavidin was immobilized and the functionalized dots were incubated with fluorescent biotin. The detection of fluorescence indicates that the streptavidin-biotin interaction has taken place. An analysis algorithm was developed which allows to discriminate fluorescence coming from the hydrogel dot and from the polymeric substrate, eliminating non-specific fluorescence from the analysis.

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### Figures



**Figure 1:** Representation of the experimental design. The hydrogel dots contain immobilized streptavidin, which is detected by binding of fluorescent biotin.

## Nanostructured thick electrode strategies

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### Abstract

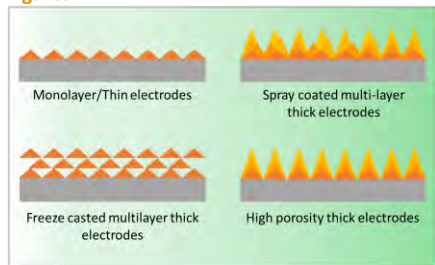
This poster addresses the issue of bulk electrode design and the factors limiting the performance of thick electrodes. Indeed, one of the challenges for reaching improved performances in electrochemical energy storage devices (batteries or supercapacitors) is the maximization of the ratio between active to non-active components while maintaining ionic and electronic conductivity of the assembly. When it comes to the development of better ESS, for instance, emphasis is made on electrode composition, especially on the nature of the active phase, its microstructure and reactivity. Whether it is rechargeable batteries or supercapacitors, electrodes are invariably fabricated as thin solid coatings on thicker current collectors. It is evident that this is not an optimal design. Yet, the implementation of thicker electrodes has traditionally run into dead ends, either by failing to provide good performance with the same formulations used in the manufacturing of conventional thin electrode or by designing thicker but ultra-sophisticated nanostructures difficult to scale up and implement. Therefore, it is necessary and urgent to tackle the need for thicker electrodes through fundamental studies which could help understand the factors hampering their performance.

In this study, we develop and compare supercapacitor thick electrodes using commercially available carbons and utilising conventional, easily scalable methods such as spray coating and freeze-casting. We also compare different binders and conductive carbons to develop thick electrodes and analyse factors that determine the performance of such thick electrodes such as porosity and tortuosity. The spray-coated electrodes showed high areal capacitances of 1,428 mF cm<sup>-2</sup> at 0.3 mm thickness and 2,459 F cm<sup>-2</sup> at 0.6 mm thickness.

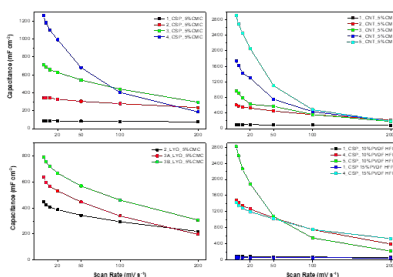
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### Figures



**Figure 1:** Schematic of multilayer electrodes structure impacting tortuosity



**Figure 2:** Areal capacitance at different scan rates for different thick electrodes.



## High yield hydrogen production enabled by macroporous silicon monoliths

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### Abstract

A macroporous silicon (MPS) membrane of 210  $\mu\text{m}$  thickness was functionalized and evaluated for hydrogen production by steam reforming of various fuels. Performance is comparable to conventional reactors, but in a much compact device thanks to process intensification [1]. No blockage or damage was observed after extensive testing. MPS technology [2] is well suited for applications as demonstrated in [3], as it allows the fabrication of large arrays of regular pores in a silicon substrate. The fabricated samples consist of an array of ordered pores of 3.3  $\mu\text{m}$  in diameter and 210  $\mu\text{m}$  length, with a straight profile; the array periodicity is 4  $\mu\text{m}$ . The as-etched sample was post-processed to create an open membrane, and later, it was conformally covered with a  $\text{CeO}_2$  film, which was then coated with a layer of RhPd nanoparticles. Different fuels were studied for hydrogen generation at high temperatures (up to 1023 K): ethanol, propanol, acetone, acetic acid, 2-methoxyethanol, and a diesel surrogate [4]. Total tests duration was 80 h. The results show that no structural damage nor channel blockage is present. Results of  $\text{H}_2$  production are shown in **Fig. 1**. The reaction hydrogen yield and selectivity show the best results for 2-methoxyethanol at 923 K, with 53% selectivity,  $\theta_{\text{H}_2} = 0.4$  yield, and a  $\text{H}_2$  production density of  $110 \text{ L}_\text{N} \text{ H}_2 / \text{mL}_{\text{fuel,liq}} \cdot \text{cm}^3_{\text{react}}$ .

Comparable results in hydrogen production with respect to conventional ceramic honeycombs have been obtained, but in a much smaller volume. Good performance was obtained and no damage or blockage was observed after extended testing, making this technology an outstanding candidate for energy production in embedded applications.

### Acknowledgements

This work has been funded by project MICINN PID2021-124572OB-C31.

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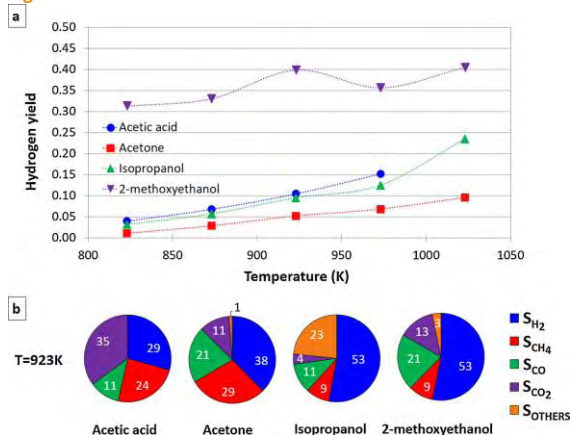


Figure 1: (a) Hydrogen yield and (b) selectivity at 923 K for different tested fuels.

## Stability of gold nanoparticles coated with detection antibody used in immunoassays

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In many immunodiagnostic technologies, the antibodies are coupled to micro- or nanoparticles. The bio-functionalized particles are used for specific capture of biomarkers and can also be used as labels in a subsequent detection step. One example is the use of gold nanoparticles due to their plasmonic properties. The process of anchoring antibody molecules to the surface of gold nanoparticles is complex and involves a balance between the need to bind the antibodies to the nanoparticle surface, and the need to maintain the biologically active molecular conformation of the antibodies to that antigen capture can occur [1]. In addition, the stability of immunoassay reagents is a requirement for validating immunoassay performance [2]. Therefore, the stability of these antibody-coated nanoparticles is essential, i.e. they must have the ability to retain their original behavior and properties over a period of time when stored under defined conditions.

In order to study this validation requirement, accelerated tests were performed, which consisted of storing the antibody-coated nanoparticles at 37°C. Through this study, it has been determined that the storage buffer is essential for the stability of these nanoparticles, observing poor stability when Bovine Serum Albumin (BSA) is used as storage, and great stability when mPEG-SH is used as storage. Additionally, it has been observed that storage can affect the variability of the immunoassay (Figure 1). Therefore, these accelerated stability assays are essential to study the immobilization protocol of antibodies on gold nanoparticles.

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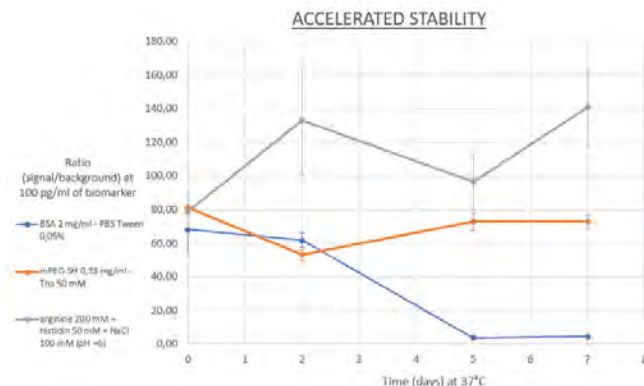
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### Figures

**Figure 1:**

Signal/ /background ratios at 100 pg/mL biomarker in an immunoassay performed with antibody-coated gold nanoparticles stored at different times at 37°C with different buffers:

- BSA 2 mg/ml – PBS Tween 0,05%.
- mPEG-SH 0,33 mg/ml – Tris 50 mM.
- Arginine 200 mM + histidine 50 mM + NaCl 100 mM (pH = 6).



## Hybrid Structures Based on Nanoporous Anodic Alumina for Optical Detection of Alcohol-Containing Fluids

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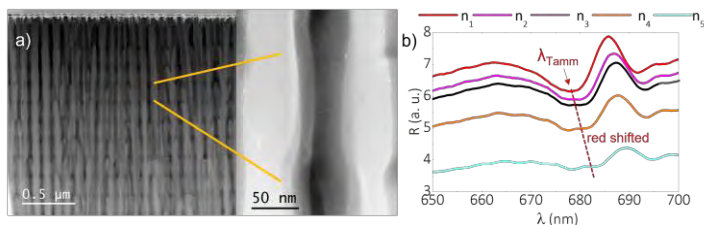
The use of hybrid metal/dielectric nanostructures has inspired the use of Tamm plasmon resonance in the design of novel optical detection systems. In this work we combined materials with plasmonic and photonic properties for this purpose. For this purpose, we fabricated gradient-index filters based on nanoporous anodic alumina (GIF–NAA) using the pulse-like anodization nanofabrication technique with sinusoidal current density profile and coated the fabricated samples with gold using the sputtering technique<sup>1</sup>. This material is a one-dimensional photonic crystal made of aluminium oxide<sup>2–4</sup>. The sensing capabilities of our samples (Au–coated GIF–NAA) were examined by monitoring the Tamm plasmon resonance in surface adsorption experiments using the reflectometric interference spectroscopy (RiS) technique. The experiments were developed in a flow cell in real time by infiltrating various alcoholic fluids into the nanopores. The results highlight the application of Au–coated GIF–NAA as a potential platform for optical sensing of volatile organic compounds by monitoring the Tamm plasmon resonance.

### Acknowledgments:

This work was supported by the Spanish Ministerio de Ciencia e Innovación (MICINN/FEDER) PDI2021-128342OB-I00, by the Agency for Management of University and Research Grants (AGAUR) ref. 2021-SGR-00739, by the Diputació de Tarragona (DIPTA) 2022/33, and by the Catalan Institution for Research and Advanced Studies (ICREA) under the ICREA Academia Award. Prof. Abel Santos thanks the support provided by the Australian Research Council through the grants DP200102614 and DP220102857.

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**Figure 1:** a) Cross-section TEM image of Au–coated GIF–NAA with magnified view of the sinusoidal nanopore created through pulse-like anodization nanofabrication technique with sinusoidal current density profile; b) Minimum wavelength in reflectance spectrum corresponding to the Tamm plasmon resonance ( $\lambda_{\text{Tamm}}$ ) is red shifted by infiltrating fluids into the nanopores created in increasing order of refractive index.

## Enhanced Stability through Conjugated Polymer Electrolyte Interlayer in Organic Solar Cells

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### Abstract

Advancing the Performance and Long-Term Stability of Organic Photovoltaics through Novel Engineering Strategies: A Study of Non-Fullerene Small-Molecules Acceptors (NFAs) and Conjugated Polymer Electrolyte Interlayers[1, 2]. While the power conversion efficiency (PCE) of OPVs has improved significantly in recent years, achieving 18% efficiency in single-junction devices, long-term operational stability remains a critical challenge for commercialization[3, 4]. To address this, various engineering strategies have been investigated to improve OPV stability and minimize intrinsic degradation. One such approach involves assessing the stability of the electron and hole transport layer materials and their compatibility with the active layer and electrodes. In this study, we examine the degradation of conventional OPVs using CPE-Na as a protective layer for the anode electrode to prevent the corrosion of PEDOT:PSS. Our fabricated structure, ITO/CPE-Na/PEDOT:PSS/PM6:Y7/PDINO/Ag, demonstrates the potential of the bilayer CPE-Na/PEDOT:PSS as a promising electrode for highly stable NF-OPVs. Normalized PCE% analysis over time shows that the cells with the bilayer maintain over 94% efficiency compared to the reference cell that uses PEDOT:PSS as a single HTL, which only maintains 83% efficiency by the end of the analysis period

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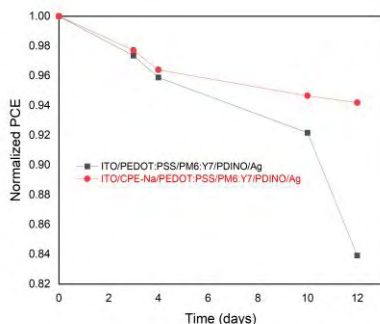


Figure 1: Normalized PCE over time

## Heteroatom Substitutions in Graphene Nanoribbons: One-dimensional Spin Chains with Tuneable Interactions

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Graphene nanoribbons (GNRs), low-dimensional platforms for carbon-based electronics, show the promising perspective to also incorporate spin polarization in their conjugated electron system. However, these magnetic moments are usually localized around zigzag edges, difficult to fabricate and very reactive. This combined theoretical and experimental study demonstrates that magnetism can also be induced away from physical edges through atomically precise engineering of topological defects in its interior. A pair of substitutional boron atoms inserted in the carbon backbone of the 7-armchairGNR breaks the conjugation of its topological bands and builds two spin-polarized boundary states around them. Therefore, a spin moment of 2 Bohr magnetons localizes around each pair of B atoms in the structure (see Figure 1).

First indications of the presence of magnetism were given by the appearance of characteristic Kondo peaks in electrical transport experiments performed at nanoGUNE. Transport was measured through boron-substituted GNRs suspended between the tip and the sample of a scanning tunneling microscope (STM). These observations were rationalized in terms of the theory and first-principles simulations performed at CFM and DIPC, which predicted for each isolated boron pair a S=1 spin state as well as a strong dependence on the spacing between pairs. The interaction between two of such topological defects was further explored, outlining a route to engineer topological spin chains, with the promising tunability of their magnetism by modifying their spacing [1].

Therefore, the present results demonstrate a route to embed spin chains in graphene nanoribbons, turning them into basic elements of spintronic devices. We are currently examining the effect of B substitution for other GNRs [2].

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## One step synthesis and characterization of RGO/Au NPs nanocomposites

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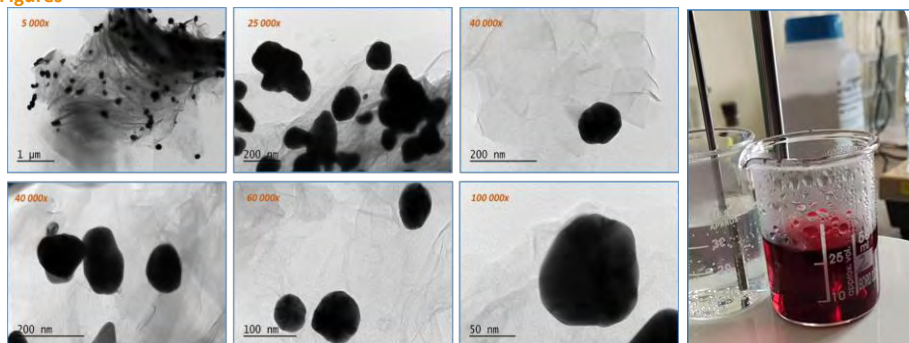
Gold nanoparticles are widely used with an important role in medicine. Graphene has wide applications in electronics and in the creation and modeling of new batteries. Graphene-based materials show great potential for electrochemical biosensor electrode materials because they increase the sensing area and improve the electron transfer rate. With the increasing demand of contemporary technological solutions, it is expected that the combination between these two materials will find an increasingly wide application in practice. RGO-AuNP can overcome the barriers that limit the potential of currently available traditional materials due to its excellent properties, which include its high specific surface area. In the present study, a single step route for the synthesis of a composite based on Au nanoparticles and RGO is proposed. The process of synthesis of Au nanoparticles from chloroauric acid ( $\text{H}[\text{AuCl}_4]$ ) and reduction using sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) takes place directly on the surface of the pre-synthesized GO layers. Through TEM and HRTEM analysis, the deposition of well-shaped spherical Au nanoparticles on the surface of the graphene layers is observed. In addition, the RGO sheets are well defined in the TEM images. The size of Au nanoparticles in the graphene composite has been determined to be in the range of 2 to 20 nm. The proposed explanation for the size difference is the formation of aggregates of different sized Au nanoparticles. The crystal lattice parameter of the obtained Au nanoparticles has been determined to be 4.07825 Å by Selected Area Electron Diffraction (SAED). Spherical gold nanoparticles with size 2-5 nm have been observed by High-resolution transmission electron microscopy (HRTEM).

**Acknowledgments:** The authors acknowledge the financial support of the National Science Fund of Bulgaria, Project KP-06-H27/17 17.12.2018.

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### Figures



**Figure 1:** TEM analysis of AuNPs/RGO composite.

**Figure 2:** AuNPs/RGO composite.

## Optimizing core-satellite superstructures as highly bright SERS-encoded particles

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Near-field coupling between localized surface plasmon resonances of individual nanoparticles is at the heart of the unique optoelectronic properties of nanoparticle assemblies.[1] Such properties can be tailored via rational design of well-defined plasmonic architectures built from metallic units of specific composition, shape, and size.[1] Production of high-quality nanoparticle assemblies with tunable plasmonic responses is one of the most exciting and fast-moving areas of nanomaterial research with a vast impact on medicine, sensing, and catalysis.[2] Remarkably, plasmon coupling of closely-spaced nanoparticles concentrates giant electromagnetic fields at the interparticle gap.[1] This unique phenomenon is often exploited by plasmon-enhanced spectroscopies, such as surface-enhanced Raman scattering (SERS) to maximize the amplification of molecular optical responses.[3] Among different morphologies, core-satellite superstructures are particularly suited to be used as plasmonic constructs in SERS as they can concentrate in a small volume a dense collection of hot-spots symmetrically arranged. Thus, this class of assemblies potentially fulfils all requirements in terms of brightness (i.e.; high SERS activity), feasibility for optically linear quantitative determination, and implementation in size-limiting applications such as in vivo and in vitro bioimaging. However, fabrication strategies have been traditionally inefficient in the production of core-satellite constructs as plasmonic substrates. Recently, we described a novel and versatile approach to generate SERS encoded core-satellite particles with minimal interparticle distances (<2–3 nm) and maximum satellite loading (i.e., maximum number of hot spots per assembly).[4] In this new study, we build on these previous findings to focus on the optimization of the SERS performances of core-satellite particles at different excitation wavelengths (i.e., 514, 633, and 785 nm) while employing diverse building blocks of different plasmonic materials to generate multiple classes of assemblies.

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### Figures

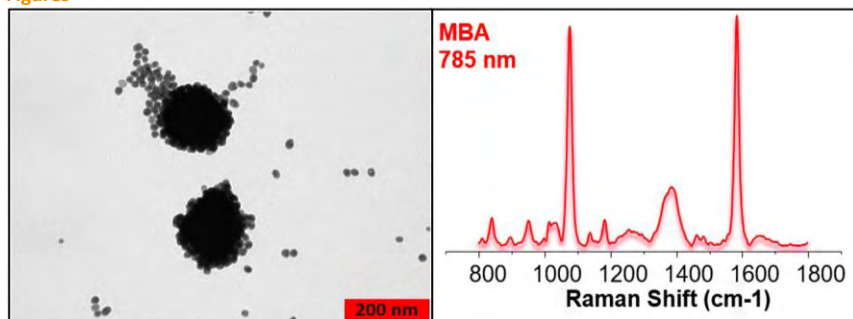


Fig. 1. Representative TEM image Au@Ag core-satellites and corresponding SERS spectra of 4-mercaptobenzoic acid encoded in Au@Ag core-satellites (excitation wavelength = 785 nm).



## Nanoporous carbon from egg white biomass for efficient Capacitive Deionization

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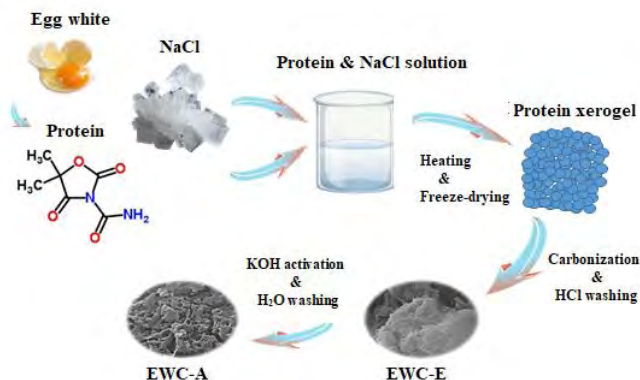
Freshwater scarcity due to rapid population growth and industrialization accentuates the issue of sustainable water recovery. Capacitive Deionization (CDI) has emerged as an efficient, energy-saving approach for brackish water desalination<sup>1</sup>. Among several factors that can affect desalination efficiency, the nature of electrode materials plays a pivotal role. Porous carbon derived from biomass has drawn increasing research attention due to the ease of fabrication, low cost, and sustainability of carbon produced from biological precursors<sup>2</sup>. However, challenges remain in processing techniques to achieve high carbon yield and tunable morphology, which requires a clear understanding over the chemical and elemental compositions as well as the structural characteristics of bio-based precursors<sup>3</sup>.

In the present study, nanoporous carbon was successfully synthesized by a two-step method involving carbonization and chemical activation using egg white as a raw material, as illustrated in Figure 1. Structure characterization showed a honeycomb morphology with an extensive three-dimensional network of interconnected macropores and mesopores. The final material exhibited high specific surface area (1547 m<sup>2</sup>/g), high pore volume (2.21 cm<sup>3</sup>/g) and tight control over mesopore size as revealed by the BET and BJH analysis. Nanocomposite electrodes were then prepared by depositing carbon slurry on graphite substrates in the form of coating. Batch-mode electrosorption experiments were carried out in a lab-scale CDI cell to evaluate the desalination performance of the electrodes. Nanocomposite electrodes showed a significant electrosorption performance with specific capacitance of 480 mF/cm<sup>2</sup> (at 2 mV/s), salt adsorption capacity of 7.4 mg/g and current efficiency of 95% at 1.2 V in 300 ppm NaCl solution. The outcome was ascribed to the intrinsic properties including high specific surface area of carbon produced making it highly attractive as electrode material.

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**Figure 1:** Detailed synthesis process of egg white-derived activated carbon, EWC-A

## Utilizing Magnesiothermic CO<sub>2</sub> Reduction to Tailor the Surface Composition of Highly Porous Carbon Nanoparticles

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### Abstract

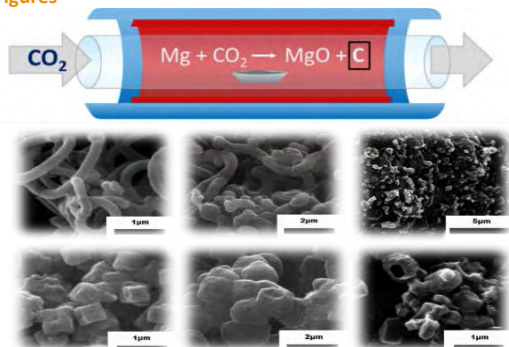
Persistently growing greenhouse gas emissions and the resulting threat to our everyday life conditions have stimulated intensive research for sustainable technologies. Progress has been made in scientific research for CO<sub>2</sub> management, and CO<sub>2</sub> conversion into value-added products has been proposed as a viable and high promising solution.<sup>1</sup> At the same time, carbon nanomaterials exhibit a combination of properties which makes them suitable for a wide range of applications, thus accelerating the demand in industry for this kind of materials. Metallothermic process, utilizing alkaline-earths and CO<sub>2</sub> as feedstock, is an emerging route to produce carbon nanomaterials.<sup>2,3</sup> In this work, Mg metal powder is heating up to 675°C into a quartz tube furnace, under constant CO<sub>2</sub> flow and atmospheric pressure conditions to form a combination of MgO and carbon nanoparticles (Fig.1). Carbon is isolated after washing in HCl solution. Adding organic compounds such as Melamine and Thiourea along with Mg metal powder, highly porous N, S and O tunable doped carbon nanoparticles have been obtained. The resultant materials' physicochemical properties were evaluated by X-Ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS) elemental analysis and Raman spectroscopy. Scanning electron microscopy (SEM) reveals the presence of both fibril and cubic carbon structures with controllable textures.

The electrochemical performance of those carbons was evaluated in neutral aqueous electrolyte (Na<sub>2</sub>SO<sub>4</sub>, 0.5M) using a three-electrode configuration consisting of porous carbon, Pt foil and Ag/AgCl as working, counter and reference electrode, respectively. Electrochemical measurements revealed that the activated porous carbon exhibited remarkable electrochemical performance with capacitance of 593.45 F/g at 20 mV/s and 328.05 F/g at 100 mV/s within a large voltage window. This outcome was ascribed to the intrinsic properties of produced nanocarbons, including -N, -S doping and high BET surface area (1996 m<sup>2</sup>/g), making them promising candidates for electrochemical applications.

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### Figures



**Figure 1:** Schematic representation of metallothermic reduction reaction and corresponding SEM micrographs from resulting carbon nanoparticles.

## Biologically Active Collagen/Reduced Graphene Oxide/Fucoidan Nanocomposites

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Collagen-based biomaterials with antimicrobial activity are attractive candidates for variety medical applications like tissue engineering, components of implantable devices, wound dressing and healing, functional coatings, etc. Development of composites that include antimicrobial agents is one of the easiest and most effective ways to add antimicrobial activity. Having for the sharply increasing microbial resistance to the conventional antibiotics and multi-drug treatments, this investigation combines such an easy approach with use of some newly synthesized, biologically active chemical compounds, plant extracts and their combinations. Here are presented collagen/reduced graphene oxide (RGO)/fucoidan nanocomposites, demonstrating antimicrobial activity that is specific toward different microbial species. and dependent on the fucoidan concentration. As compared to that of the collagen/RGO nanocomposites, their activity against Gram-positive bacteria (*L. inoculae* and *B. cereus*) and fungus (*C. lusitaniae*) is increased. Furthermore, the missing activity against Gram-negative bacteria (*P. putida*, *S. enterica*, *P. aeruginosa*, and *E. coli*) in absence of fucoidan is moderate in its presence and the cytotoxicity to eukaryotic cells is low. The different activity toward different test microbial species and eukaryotic cells was attributed to their specific morphology and size. With a wide spectrum, specific and adjustable bioactivity, the new collagen/RGO/fucoidan nanocomposites are promising antimicrobial biomaterial for variety biomedical applications.

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