

2021 NANO PORTUGAL

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Abstracts Book



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Foreword

On behalf of the Scientific and Technical Committees we take great pleasure in welcoming you to the second edition of the nanoPT International Online Conference (NPTO2021).

The two-days NPTO2021 will present the most recent advances in fundamental research & technology developments in Nanoscience and Nanotechnology (N&N). This event is launched following the success of previous nanoPT editions (in-person & online) and considering that all major scientific and technological conferences are being cancelled or postponed worldwide until the end of 2021.

NPTO2021 will be held with the purpose of strengthen ties nationally and internationally on Nanotechnology and will encourage companies and public institutions working on the Nanotechnology field to know each other and to present their research.

More than 20 high profile worldwide most influential academia/industry experts in the N&N sector will present speeches in this international event on how advanced materials will change the future of technology and impact positively our daily life in sectors such as Energy, Electronics or Biohealth.

In addition, thanks must be given to the staff of all the organising institutions whose hard work has helped planning this conference.

We would like to thank all participants and speakers that joined us this year. Hope to see you again in the next edition of the International nanoPT Conference in 2022, hopefully in-person.



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Abstracts Keynote

Advances in the large-scale production of 2D crystals

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Abstract

Nowadays is of utmost importance the development of industrial-scale, reliable, inexpensive production processes of graphene and related two-dimensional materials (GRMs).[1,2] In fact, this is a key requirement for their widespread use in several application areas,[1-6] providing a balance between ease of fabrication and final product quality. In particular, in the energy sector, the production of GRMs in liquid phase [2,6] represents a simple and cost-effective pathway towards the development of GRMs-based energy devices, presenting huge integration flexibility compared to other production methods.

In this presentation, I will present the strategy of BeDimensional in the production of GRMs by wet-jet milling [7] and the Industrial scale up. Afterward, I will provide a brief overview on some key applications of the as-produced GRMs, for anticorrosion coatings and energy conversion[3,8-11] and storage[8,12-16] devices.

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Defect-free and Biocompatible 2D Material Inks for Printed Electronics

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Solution processing of 2D materials allows simple and low-cost techniques, such as ink-jet printing, to be used for fabrication of heterostructure-based devices of arbitrary complexity. However, the success of this technology is determined by the nature and quality of the inks used.

Our group has developed highly concentrated, defect-free, printable and water-based 2D crystal formulations, designed to provide optimal film formation for multi-stack fabrication [1]. We have demonstrated printed photosensors on plastic, programmable logic memory devices, capacitors, transistors, high-gain inverters, logic gates, and current mirrors [1-4]. Our graphene ink also enables fabrication of visco-elastic electrodes for soft tissues, such as the brain [5]. Finally, cytotoxicity tests confirm biocompatibility of the 2D material inks [1]; in particular, cationic graphene dispersions produced with our approach show exceptional intracellular uptake profile as well as stability in the biological medium, making this type of graphene very attractive for use in nanomedicine [6].

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A biophysical study of an extracellular matrix bacterial protein

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Abstract

Functional amyloid proteins are self-secreted by microbial cells that aggregate into extracellular networks and provide microbial colonies with mechanical stability and resistance to antibiotic treatment. In order to understand the formation mechanism of functional amyloid networks, their aggregation has been studied *in vitro* under different physical conditions, such as temperature, salt concentration, and pH. Typical aggregates' morphologies include fibers or plaques, the latter resembling amyloid aggregates in neurodegenerated brains. Here, we studied the effect of salt concentration and solution pH on the aggregation process of TasA, an extracellular functional amyloid protein appearing as fibers in biofilms of the soil bacterium, *Bacillus subtilis*. We used turbidity and zeta potential measurements, Electron Microscopy, Atomic Force Microscopy, and static light scattering, to characterize the aggregates of TasA. Based on these studies, we suggest two possible aggregation mechanism of TasA *in vitro*. In acidic pH conditions, TasA aggregation is fast and it resembles colloidal aggregation, whereas in the presence of high salt concentrations, TasA aggregation is slower, yielding straight and long-range structured fibers. Shedding light on the aggregation mechanism of TasA, our results can be used for the design of TasA aggregation inhibitors and promoters.

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FIGURES

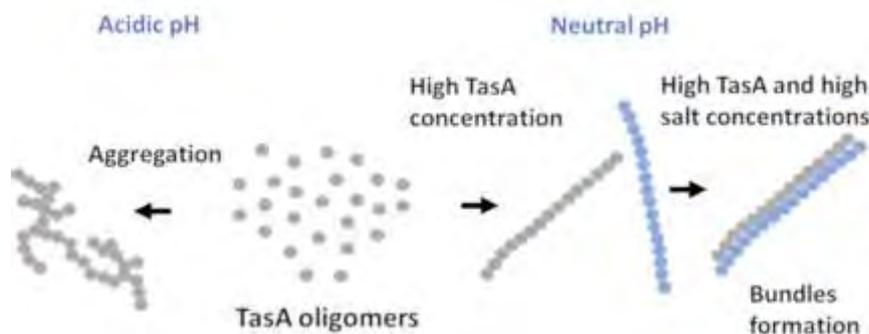


Figure 1: TasA aggregation pathways in different environmental conditions.

Low-dimensional materials as platform for sensing and water purification

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Low-dimensional materials (LDMs) exhibiting a high surface-to-volume ratio are unique scaffolds whose interactions with the environment drive their application as sensitive elements in chemical sensing. They allow prompt reconfiguration of the architectures of the sensor, whose response to the detection of chosen analyte becomes no longer limited by extrinsic factors such as the slow diffusion of target molecules through the active material or the presence of structural traps for small molecules/ions. The unique features of LDMs determine the highest responsiveness, sensitivity, and reversibility combined with the lowest limit of detection (LoD) in the sensing process.

Pristine LDMs are being widely exploited as highly sensitive elements in chemical and physical sensors, although they suffer from the lack of intrinsic selectivity towards specific analytes. Here, we showcase the most recent strategies explored in our laboratory on the use of (supra)molecular interactions to harness selectivity of suitably functionalized 0D and 2D materials for chemical and physical sensing. We discuss how to achieve selectivity in chemical sensors along with other relevant characteristics, such as high sensitivity, response speed, and reversibility, by suitable functionalization and incorporation of low-dimensional materials into powerful transducers.

We will discuss piezoresistive pressure sensor based on a millefeuille-like architecture of reduced graphene oxide (rGO) intercalated by covalently tethered molecular pillars holding on-demand mechanical properties are fabricated. By applying a tiny pressure to the multilayer structure, the electron tunnelling ruling the charge transport between successive rGO sheets yields a colossal decrease in the material's electrical resistance.

We will also discuss novel generation of humidity sensors based on a simple chemical modification of rGO with hydrophilic moieties, i.e., triethylene glycol chains. Such a hybrid material exhibits an outstandingly improved sensing performance compared to pristine rGO such as high sensitivity (31% increase in electrical resistance when humidity is shifted from 2 to 97%), an ultrafast response (25 ms) and recovery in the subsecond timescale, low hysteresis (1.1%), excellent repeatability and stability, as well as high selectivity toward moisture.

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Organic Chemistry meets quantum magnetism

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In this talk I will discuss how a special class nanographenes can be used to **as building blocks for artificial quantum spin models**. These nanographenes are open-shell (or diradical) planar aromatic hydrocarbons. In conventional organic chemistry they are highly reactive and hard to study. Combining on-surface synthesis techniques in ultra-high vacuum and scanning tunnelling microscopy it is possible to study this fascinating class of molecules. In this talk I will focus on [n]-triangulenes¹, nanographenes with the shape of an equilateral triangle with lateral dimension of n benzenes. These triangulenes have a magnetic ground state with spin $S=(n-1)/2$. Thus, 3-triangulenes have $S=1$ ². We recently showed³ that [3]-triangulene dimers are coupled antiferromagnetically, with a strong exchange of 14 meV. This sets the stage for the formation of larger structures including chains and rings of antiferromagnetically coupled $S=1$, that permit to demonstrate one of the cornerstones of quantum magnetism, the Haldane phase of spin chains, as we reported recently⁴. I will also discuss the prospect to explore other quantum spin models based on triangulene arrays.

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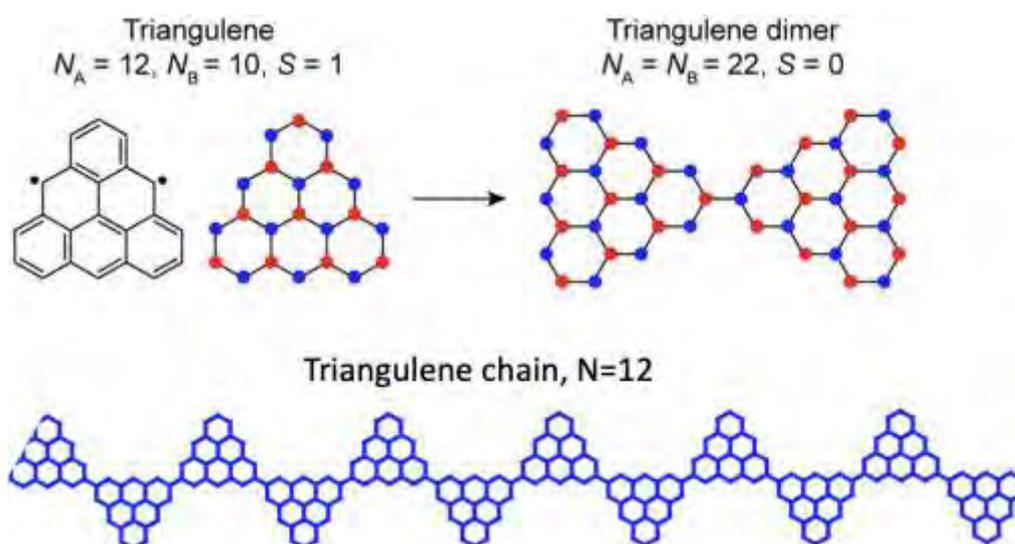


Figure 1: Top panels, from reference[3]: triangulene monomer (left) and dimer. Bottom: chain of 12 triangulenes, forming a $S=1$ spin chain that realizes the Haldane phase⁴.

Understanding the Structure of LiMn_2O_4 by Aberration-Corrected HAADF STEM and Differential Phase Contrast

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Abstract: The rising need for portable energy storage has led to the creation of a formidable Li-ion battery industry, which is poised to grow strongly in the near future. Of the many cathode chemistries for Li-ion batteries, $\text{Li}[\text{Mn}_2]\text{O}_4$ (LMO) stands out as a particularly appealing cathode due to its moderate capacity, use of environmentally-friendly and cost-effective Mn, and high rate capabilities associated with its cubic spinel framework, which allows three dimensional Li+diffusion. Yet, this material has shown capacity loss, attributed to the dissolution of Mn to the electrolyte. In this work we show by HAADF STEM that a restructured surface is formed in this material, where a stable surface layer of Mn_3O_4 , followed by $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ subsurface with retention of bulk LiMn_2O_4 is formed. In addition, recent advances in STEM allow us to observe not only the structure of the materials at atomic level, but also to obtain images proportional to the projected potential, the projected electric field and the projected charge distribution, by using differential phase contrast technique (DPC). Thus, in this work we also use DPC to determine the Li, Mn and O atomic positions, thus providing a novel insight into the structure of LiMn_2O_4 . Our results clearly show local regions depleted in Li and the existence of manganese atoms in tetrahedral sites occupying a typical Li atom position, or occupying a free octahedral site in the same column, in agreement with the Mn disproportionation reaction reported for such compound. These findings contribute to a better understanding of the mechanisms of lithium and manganese exchange in LiMn_2O_4 spinel structures.

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FIGURES

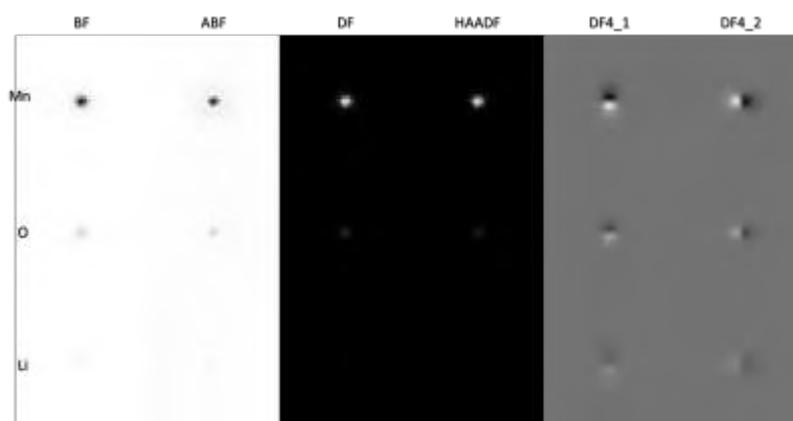


Figure 1: BF, ABF, DF, HAADF and DPC signals for manganese, oxygen and lithium.

Renewable materials applied to electronics

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Today there is a strong interest in the use of sustainable materials and in some cases, materials from renewable origin for electronic applications, driven by the development goals as well as by low-cost applications. One of the most representative examples is cellulose, not only in the form of raw material mainly for pulp and paper production, but also in the development of advanced materials/products with tailor-made properties, especially the ones based on nanostructures.

Paper offers a cheap, flexible and biodegradable alternative substrate to silicon for simple electronic devices like disposable sensors. Office copy paper is 10,000 times cheaper than silicon, but it also avoids the problems of electronic waste.

Another advantage of paper relies on its biodegradability and thus its use can release some of the urgent issues and challenges of the electronic waste management.

Indeed, although paper electronics cannot compete with silicon-based electronics in complex integrated circuits, simpler electronic components and sensors could be fabricated on paper substrates at a sizeable lower cost and with lower electronic waste footprint. Paper flexibility also makes it particularly suitable for flexible electronics applications.

In this talk we will discuss the state of the art and potential future directions in paper-based electronics with special emphasis to the work developed at CENIMAT|i3N, covering electronic devices, smart displays, printed electronics, sensors and diagnostic tests.

From lab to farm: monitoring grape maturation and vine hydric stress with integrated optical sensing and IOT technologies

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Abstract

Within the H2020 I GRAPE project (<https://i-grape.eu>), integrated microspectrometers (from 400nm to 1500nm), front end and communication hardware, and optical data analysis models are being developed to monitor diffuse reflectance and fluorescence response from grapes and leaves. Grape maturation parameters (for example titratable acidity , potential alcohol, total polyphenols) as well as water potential in the leaf are being evaluated. The optical microspectrometer assembles chip level LEDs, integrated photodiodes (either a-Si:H or CMOS) with bandpass filters, with discrete front end electronics (or an ASIC). This optical head is placed inside the grape bunch or below the leaf. The analog front end involves both LED drivers and photodiode readout electronics (at ASIC level). The communication module uses a LORA protocol to transfer data from the vineyard to a gateway then sending the information via internet to the server. First real time data is being assessed this season.

The potential of 2D polymers for light harvesting applications

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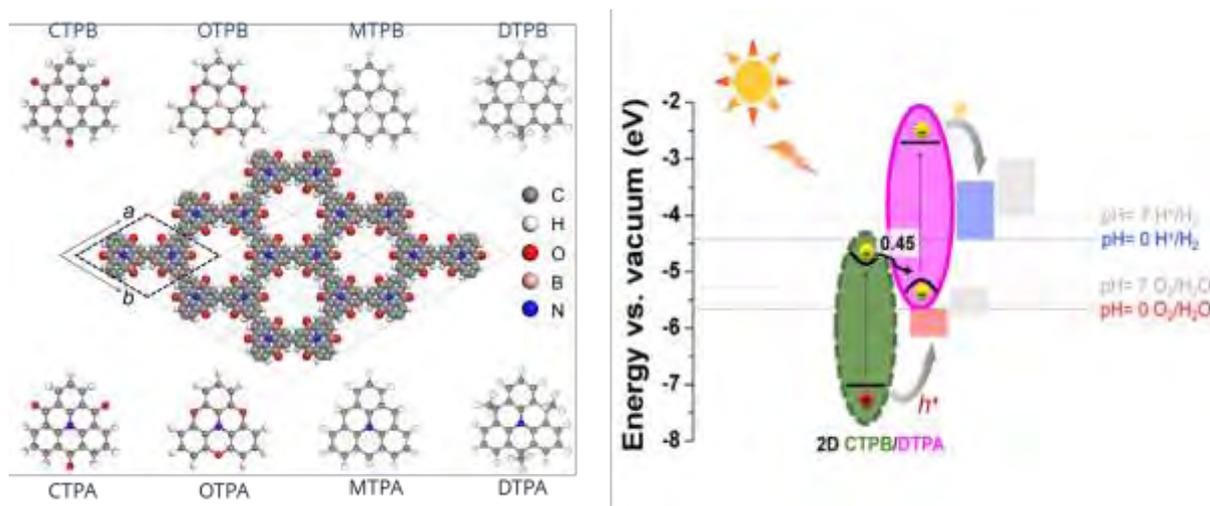
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Decentralized production of green hydrogen by solar-fueled water splitting is key for a successful transfer to a zero emission energy supply. Our goal is the development of materials that are efficient photocatalysts without additional need for infrastructure, have long-term stability, and transform a considerable part of the solar spectrum to chemical and electric energy.

To achieve this goal we take advantage of various options that are offered by conjugated 2D polymers, in particular

- full conjugation to allow for band dispersion and high charge carrier mobility
- lattice symmetry that determines electronic band structure
- functionalization to in-plane control conjugation and photocatalytic performance
- functionalization with heteroatoms to shift bands with respect to vacuum

As example system we use honeycomb-kagome structures based on hetero-triangulenes [1,2]. If designed properly, they can be arranged in tandem cells where hydrogen and oxygen evolution is spatially separated, and no additional catalyst, voltage or sacrificial agent is required-(Figure) [3].



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REASSURED paper-based nanobiosensors for diagnostics

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There is a high demand to develop innovative and cost effective devices with interest for health care beside environment diagnostics, safety and security applications. The development of such devices is strongly related to new materials and technologies being nanomaterials and nanotechnology of special role. We study how new nanomaterials such as nanoparticles, graphene, nano/micromotors can be integrated in simple sensors thanks to their advantageous properties. Beside plastic platforms physical, chemical and mechanical properties of cellulose in both micro and nanofiber-based networks combined with their abundance in nature or easy to prepare and control procedures are making these materials of great interest while looking for cost-efficient and green alternatives for device production technologies. These devices should be REASSURED: Real-time connectivity, Ease of specimen collection, Affordable, Sensitive, Specific, User-friendly, Rapid, Robust, Equipment-free, Delivered to those who need it. How to design simple paper-based biosensor architectures? How to tune their analytical performance upon demand? How one can couple nanomaterials with paper and what is the benefit? Which are the perspectives to link these simple platforms and detection technologies with mobile communication? I will try to give responses to these questions through various interesting applications related to protein, DNA and even contaminants detection all of extreme importance for diagnostics, nanotheranostics, environment control, safety and security.

Surprising Charge Transport in DNA and Properties of Novel DNA-Based Molecules

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Abstract

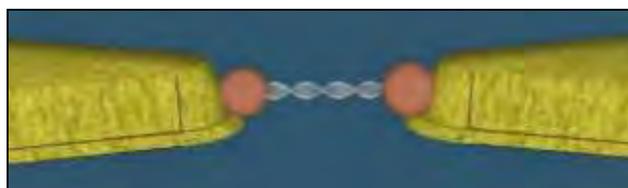
Charge transport through molecular structures is interesting both scientifically and technologically. To date, DNA is the only type of polymer that transports significant current over distances of more than a few nanometers in individual molecules. Nevertheless and in spite of large efforts to elucidate the charge transport mechanism through DNA a satisfying characterization and mechanistic description has not been provided yet.

In recent years we have invested great efforts to address the above issues. Measuring the charge transport in DNA was elusive due to great technical difficulties leading to various results. We recently devised an experiment in which double-stranded DNA is well positioned between metal electrodes. Electrical measurements give surprisingly high currents over 100 base-pairs (~30 nm) elevated from the surface. The temperature dependence indicates backbone-related band-like transport.

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FIGURES



Transport of Ions, Electrons, and Molecules across the Solid Electrolyte Interphase (SEI) in Lithium-Ion Batteries – What is our Current Level of Understanding?

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The solid electrolyte interphase (SEI) on the graphite anode of lithium ion batteries plays a crucial role for the battery performance. The SEI blocks electrons and solvent molecules, while Li^+ ions can easily migrate across the SEI. However, quantitative measurements of transport coefficients for these species in the SEI are problematic due to the complex structure of graphite composite anodes. Therefore, we have grown model-type SEIs on planar glassy carbon electrodes and have characterized them by a combination of FIB/SEM, AFM-based scratching experiments, impedance spectroscopy and redox probe experiments. FIB/SEM and AFM experiments reveal a dual-layer structure of the SEI and give indication that the inner layer is composed of agglomerated spherical particles. Impedance spectroscopy and redox probe experiment show that the effective diffusion coefficient of Li^+ ions and redox molecules in the SEI are virtually identical and, in addition, show the same temporal evolution after SEI formation and the same activation energy. Our results suggest that the inner SEI layer exhibits a small porosity, which plays a very important role for the transport. Finally, by comparing redox molecule transport and SEI growth rates, we give strong indication that redox molecules are transported much faster than the electrolyte solvent molecules.

Nanopatterning Regulates Architecture of intercellular communication during mesenchymal cell condensation

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Data from the World Health Organization indicates that musculoskeletal conditions are the leading contributor to disability worldwide affecting between 20 to 33% of people. Although many musculoskeletal conditions can be managed in primary care, some of them require of surgical intervention. In such cases, and especially in tissues with a limited capacity of self-repair as cartilage and tendon, regenerative medicine approaches became significantly relevant.

We have developed nanopatterned cell carriers of tunable cell adhesive properties that improve mesenchymal stem cell preconditioning in vitro towards cartilage tissues, showing that extracellular matrix (ECM) information propagates into chondrogenic condensates and its effect on intercellular communication during chondrogenesis.

We inhibited myosin activity and blocked integrin receptors in condensates formed on substrates with low or high ligand density, and quantified Cx43 protein production. Cx43 decreased in both cases, indicating that the mechanism driving the previously observed results is dependent on actin contractility and integrin sensing of nanopatterned ligands. This shed light into the mechanism of how matrix inputs regulate morphogenesis by propagating information into forming tissue. Preliminary results on the implantation of the obtained cell constructs in vivo show increased efficiency in the regeneration of cartilage defects.

Bioengineered nanomedicines to modulate the local and intracellular pharmacokinetics of anticancer drugs for colorectal cancer

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Our group is focused on the development of drug delivery systems, with special attention on nanotechnology, and their application to the pharmaceutical and biomedical fields. There is a particular interest in establish bioengineering targeted nanomedicines for oral delivery of anti-tumor drugs for colorectal cancer. The group also developed and validated novel in vitro cell-based intestinal model to evaluate the permeability and performance of drugs and drug delivery systems and proposed an innovative multicellular 3D colorectal cancer spheroid model used to screen efficacy of anticancer nanomedicines.

In this presentation, our most recent achievements of the establishment of micelles and polymeric-based nanoparticles, with passive and active targeting features for colorectal cancer cells will be described. Our approach involves innovative nanomedicines, with deep and comprehensive physical-chemical, in vitro and in vivo evaluation.

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Shining light on metal colloids in the trace detection of water pollutants

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Water is essential to all known life forms. The sustainable use of water resources is an unquestionable global challenge whose relevance had increased with the awareness for climate changes.[1] This is a rather complex issue requiring effective measures at very different levels but that necessarily need safe technologies to ensure water quality for all. Nanomaterials science shows great potential in this field, namely when associated to emerging point-of-care water monitoring and purification nanotechnologies.[2,3] In this lecture, the above topic is approached by presenting selected examples of our research in the chemistry of nanomaterials for water quality monitoring, in particular by discussing applications based on surface enhanced Raman scattering methods (SERS) using metal colloids.[4-6] The challenges posed in the implementation of these methods depend largely on our ability to synthesize and modify nanomaterials for target environmental applications. Thus, several chemical strategies are presented here that tackle current limitations found in this field, such as the long-term stability of homogeneous colloidal SERS substrates versus the fabrication of reproducible and low-cost solid substrates. A final discussion concerns the perspectives for real applications of SERS methods to monitor trace amounts of contaminants in complex aqueous matrices and the challenges ahead of us.

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Quantum materials design: challenges and opportunities

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Unconventional superconductivity with high critical temperatures, topologically non-trivial phases, frustrated magnetism, spin-liquids or the recently discussed Kitaev phases are a few examples of exotic states in quantum materials. One of the big challenges in quantum physics is the microscopic description of such materials. Moreover, being able to understand them implies the possibility of predicting compounds with desirable properties. In this talk, I will present and discuss strategies for designing quantum materials from first principles, with emphasis on two-dimensional topological systems (Fig. 1, Fig. 2) [1,2,3] and will motivate their possible use for present technological applications such as quantum computing purposes.

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FIGURES

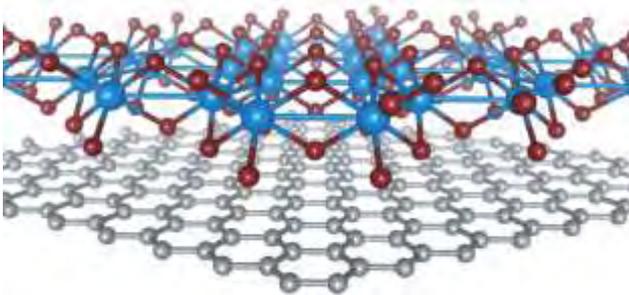


Figure 1: α -RuCl₃ in proximity to graphene

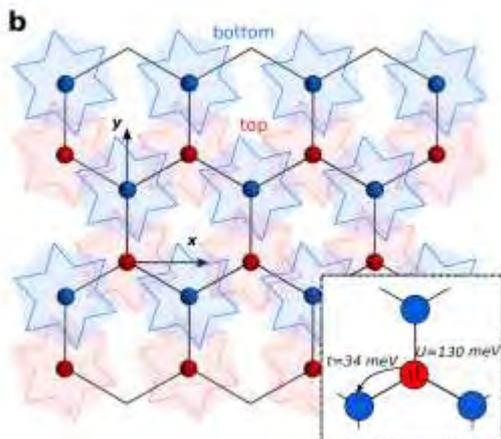


Figure 2: Stacking 1T-TaSe₂ into bilayers can deconfine electrons from a deep Mott insulating state in the monolayer to a system of correlated Dirac fermions in the bilayer.

Nanostructured electrolyte-electrode systems in next-generation batteries

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Abstract

In this talk we review the main recent advances in the nanostructured design of electrodes and electrolytes to achieve high efficiencies in electrochemical energy storage devices, specifically alkali metal batteries, redox flow batteries, and supercapacitors. The main strategies currently used to produce smartly engineered nanostructured anodes and cathodes, as well as nanoconfined ionic electrolytes (ionogels) will be treated, together with their main physicochemical properties and the essentials of the structure of the corresponding electrolyte-electrode interface.

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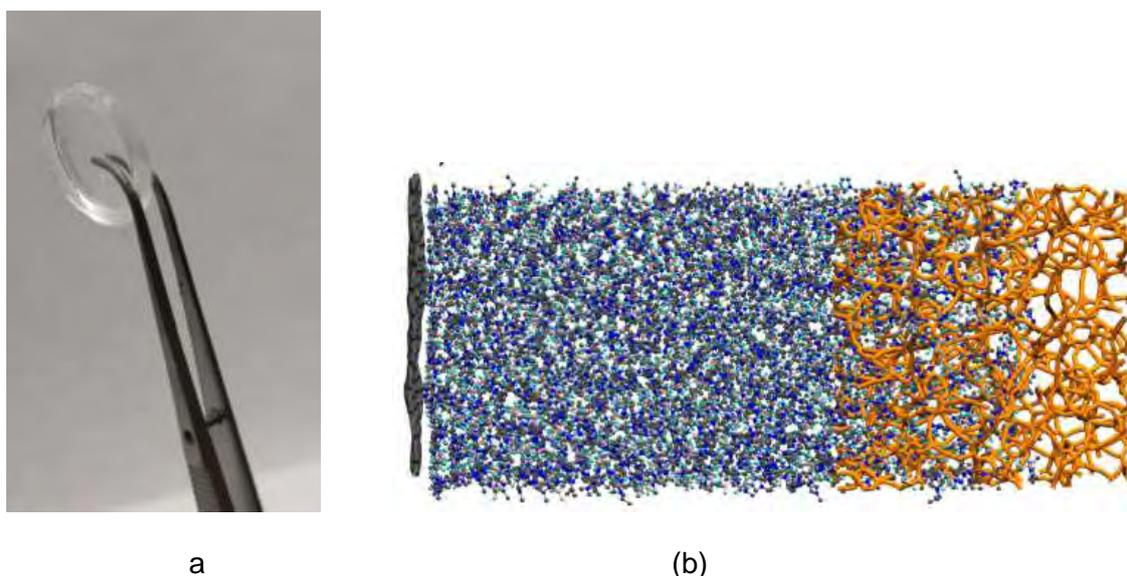


Figure 1: Nanoconfined electrolytes: (a) Si-based ionogel (IL:[TMOS:DMDMS]:FA); (b) Ionic liquid inside a zeolite template.

Sub-unit cell investigations of nanomaterials through aberration corrected electron microscopy

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The fast pace of technological development of our society continuously demands new nanomaterials for applications areas such as data storage, sensors, spintronic devices or energy applications. Functionalities of interest can result from mechanisms related to static equilibrium (crystal structure, ground state electronic properties, etc), or also from dynamic processes involving mass or electronic transport under external stimuli. For instance, an electric bias can change the local concentration of O vacancies within the lattice of oxide materials, causing structural instabilities and changes of crystal symmetry, oxygen electromigration or other processes. Other examples may include local chemical fluctuations, strong electronic correlations, unusual cooperative behaviours like high T_c -superconductivity, colossal magnetoresistance, ferroelasticity or colossal ionic conductivity. In order to harness such phenomena, we need to be able to *both visualize and quantify* atomistic phenomena in conditions similar to those found in working environments. Now, more than ever, we need to be able to watch and track the properties atoms at work. This is a task that demands real space probes that can inspect matter at the atomic scale in both static and dynamic regimes, on an atom-by-atom basis. Aberration corrected scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS) has brought sub-Ångstrom electron beams to bear on this task resulting in unprecedented sensitivity for imaging and spectroscopy, including the feasibility of mapping electric and magnetic fields at the atomic scale. This talk will review some examples of applications of these techniques to interfaces and nanomaterials. Examples include local measurements of electronic and magnetic properties of ultrathin epitaxial films based on the ferromagnetic manganite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO). STEM-EELS combined with density-functional calculations can be used to study the role of local structural distortions and electronic phenomena associated with point defects such as O vacancies on stabilizing interfacial magnetism. A second example including imaging of systems out of equilibrium can be found the study of Ni_3Fe nanoparticles for supercapacitors. Room temperature annealing in the objective lens magnetic field (close to 3T) induces a segregation of Ni and Fe species, in the form of small nanoclusters. Further heating induces Fe oxide segregation, resulting in core-shell like systems and Ni/NiO nanoclusters that have been identified as a major culprit for the pseudocapacitance enhancement. Work carried out in collaboration with G. Abellan, J. I. Beltran, E. Coronado, J. Grandal, A. Guedeja-Marron, C. Leon, S. G. Miralles, M. C. Muñoz, H. Prima-Garcia, J. Romero, J. Santamaria, J. Tornos. Research at UCM sponsored by grant# RTI2018-097895-B-C43.

Combinatory approaches against cancer based on Gold nanoparticles

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Cancer is estimated to impact more than 20 million people globally in the next years. It has been proposed that specific anti-cancer treatments should rely on combinatorial therapies targeting multiple components the disease, to minimize compensatory mechanisms that could result in relapse and resistance to treatment. Nanotechnology is expected to provide a range of tools for cancer diagnosis and treatment (theranostics) as their sizes are well matched in size to biologic molecules and cell structures. Noble metal NPs, and gold NPs (AuNPs) in particular, attract significant interest because of their ease of synthesis and functionalization derived from their large surface area to volume ratio suitable for multifunctional capacity [1]. Several strategies have been proposed based on AuNPs simultaneously functionalized with siRNA/antisense and targeting molecules (peptides, antibodies, etc) for the development of conceptual combinatory therapeutic approaches [1]. These may also profit from the intrinsic optical properties of AuNPs, which are efficacious light-to heat transducers that can be used for photothermal therapy (PTT) approaches [2]. Commonly, NIR irradiation is usually used with AuNPs, but recently, we demonstrated the potential of visible irradiation for photothermal induction using spherical AuNPs (17 nm) with a characteristic localized SPR band around 520 nm, with seemingly higher photothermal conversion efficiency [2]. Our group has been using AuNPs for combined anticancer nanotherapeutics *in vitro/in vivo*, including precise active targeting of cancer cells to deliver chemotherapeutics, gene silencing of crucial pathways involved in cancer development, and anti-angiogenic capability, which may be enhanced via photothermal induction [3,4].

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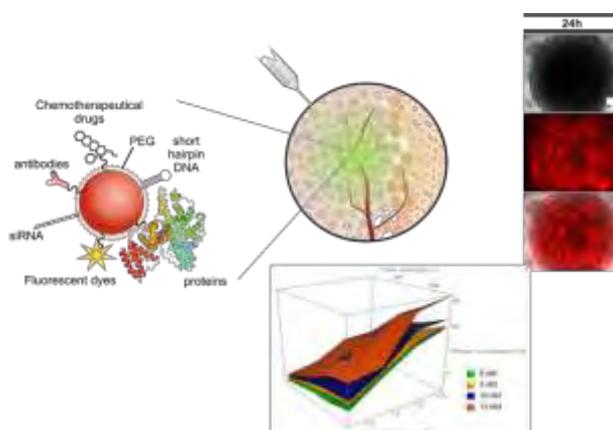


Figure 1: Multifunctional AuNPs for photothermal combinatory action against tumour cells

Abstracts Invited

Biosensing with Graphene Devices

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Graphene, a two-dimensional sheet of carbon atoms arranged in a honeycomb lattice, is an emerging material for biosensing applications [1]. Its unique electronic properties, high chemical and mechanical stability, and cyto- and biocompatibility make it especially suited for multimodal biosensing. In particular, graphene field-effect transistors (GFETs) can be set to sense ionic currents and functionalized with biorecognition elements. Our group has extended experience fabricating and testing graphene sensors for DNA and protein detection in optimized buffers and body fluids such as blood and saliva using synthetic or extracted DNA from biological samples [2,3]. We present microelectronics label-free biosensing platforms based on liquid-gate graphene field-effect transistors for DNA hybridization detection with SNP sensitivity and antigen-antibody assays with a tunable dynamic range. The systems are operated by delivering microdroplets (~10 μ L) of analyte directly onto the graphene transistor channels followed by data acquisition or by inserting the chip into a microfluidic chamber connected to a syringe pump and a multiposition valve for automated measurements. The flow system reduces in 50% signal drifts observed when using droplets. Projects based on the GFET platform with different layouts for simultaneous neurotransmitters and electrical events detection in the brain, multiplex malaria diagnostic detection of several Plasmodium species, wine authenticity control based on DNA SNP analysis, and extracellular matrix biomarkers relevant for ischemic stroke therapy are ongoing. You can learn in detail about some of these in this conference, reported by team members. In another approach, we use the z^{-4} nanoscale distance-dependence of the fluorescence lifetime for fluorophores located in the vicinity of graphene to track the hybridization of fluorescently labeled DNA beacons attached to graphene with complementary (target) DNA added in solution. In this way, we can monitor the vertical displacement of the label during DNA-beacon hybridization with an axial resolution reaching down to 1 nm [4].

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FIGURES

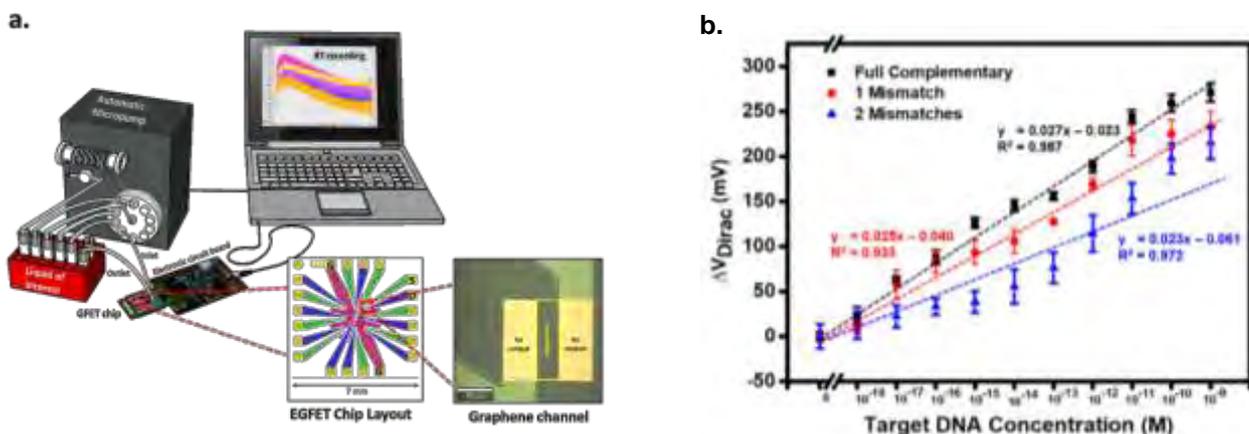


Figure 1: Set up for benchtop GFET biosensor operation coupling to a microfluidic system. b) DNA hybridization calibration plots, showing SNP sensitivity.

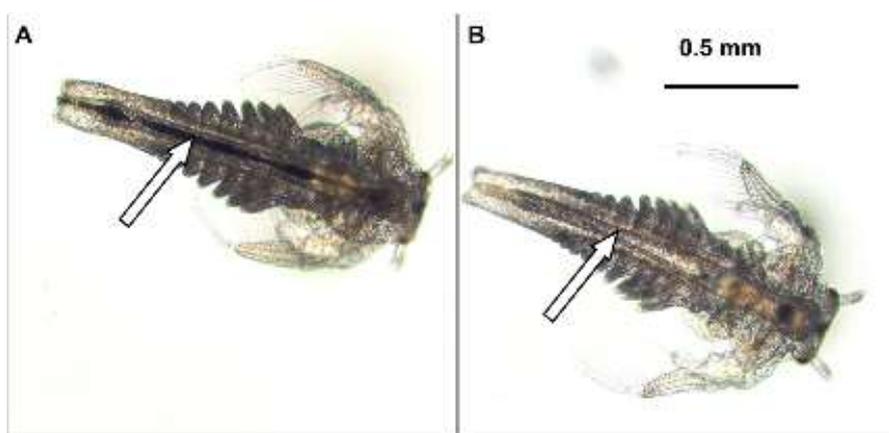
Present and future challenges of nanomaterials for the environment

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The release of nanomaterials into the environment is increasing, and more and more nanomaterials are reaching freshwaters. This is of great concern due to the potential risks for aquatic biota and functions they drive in the environment. We will discuss principal effects of nanomaterials on aquatic biota and ecosystem processes and the potential of bioaccumulation of nanomaterials along food chains. We will also discuss the EU regulation (or absence of it) to minimize the nanomaterials release and the risks to the environment and human health. We will propose measures to mitigate nanomaterial impacts on freshwaters and we will identify the players, which should be involved to minimise this problem of global concern

Fig 1: CuO nanoparticles accumulation in the gut of a freshwater organism. A) exposed to CUONPs B) not exposed.



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Electrical Control of Valley-Zeeman Spin-Orbit-Coupling–Induced Spin Precession

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The extraordinary electronic properties of graphene can be controlled by stacking it with other layered materials creating van der Waals heterostructures. In particular, graphene's low spin-orbit coupling (SOC) can be enhanced by proximity with transition metal dichalcogenides (TMDs), leading to new spin transport channels with unprecedented spin textures [1-5]. We have optimized bilayer graphene-TMD heterostructures to achieve magnetic-field-free spin precession. Additionally, by applying a drift current, we have reversed the sign of the spin signal [8]. Our unprecedented observations represent the first realization of electrical control of SOC-induced spin precession at room temperature, a crucial requirement for spin-based logic operations that can enable a new generation of multifunctional spintronic devices.

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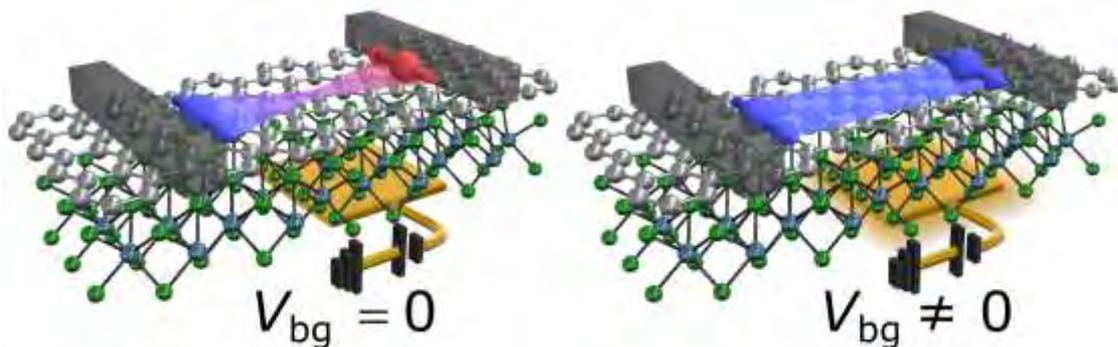


Figure 1: Schematic illustration of the device operation. At zero gate voltage (V_{bg}), the spins are reversed (left panel), whereas at nonzero V_{bg} spins are not reversed (right panel).

Development of thermal microtransducers for integration in Organ-on-a-chips

Graça Minas

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The integration of microtransducers in an organ-on-a-chip platform is essential to real-time monitoring the physicochemical properties of the organ model and keep a well-controlled microenvironment to provide optimal conditions for cultured cells, mimicking the human body [1]. Moreover, it will add essential information for the screening of new drugs, by assessing the dynamic responses of the organ-on-a-chip to pharmaceutical compounds for long-term studies, providing an accurate prediction of human organs reactions. Here we discuss the design, fabrication and characterization of temperature and heating microsensors directly on the cell models [2], as well as in the microfluidic system to monitor the feed fluid, enabling the determination of the toxicological and/or therapeutic effect in three-dimensional (3D) models of human organs.

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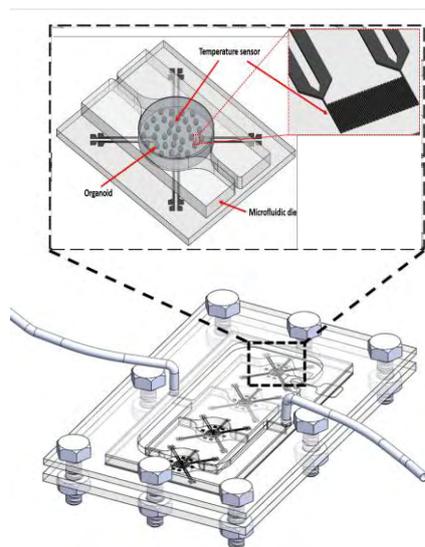


Figure 1: Schematic representation of the microsensors integrated in the organ-on-a-chip

Proof-of-Concept Study of Gold-based Nanosystem Combined with NIR Laser Irradiation for Melanoma

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The global impact of cancer emphasizes the importance of developing innovative, effective and non- or minimally invasive therapies. Photothermal therapy (PTT) is attracting increased attention for the treatment of superficial localized tumors, relying on the induction of local hyperthermia of tumor cells upon their irradiation with light beams. PTT efficacy depends, however, on the heat generated and, on the depth reached by the light. Some strategies to improve PTT efficacy includes the use of the near infrared (NIR, 650 to 900 nm) radiation to enhance the penetration depth of the light, combined with gold nanoparticles to enhance the photothermal effect. The development of a multifunctional nanoparticle-based system and its *in vitro* and *in vivo* safety and efficacy characterization are, herein, proposed as a proof-of-concept. This multifunctional system consists of coated gold nanoparticles [1-2] and functionalized with epidermal growth factor for greater specificity towards cutaneous melanoma cells [3]. The characterization of this system included several phases [4], with *in vitro* assays being firstly performed to assess the safety of gold nanoparticles without laser irradiation. Then, hairless immunocompromised mice were selected for a xenograft model upon inoculation of A375 human melanoma cells. Treatment with near-infrared laser irradiation for five minutes combined with *in situ* administration of the nanoparticles showed a tumor volume reduction of approximately 80% and, in some cases, led to the formation of several necrotic foci, observed histologically. No significant skin erythema at the irradiation zone was verified, nor other harmful effects on the excised organs. In conclusion, these assays suggest that this system is safe and shows promising results for the treatment of superficial melanoma.

ACKNOWLEDGMENTS

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Abstracts Oral

Attomolar label-free dopamine detection with aptamer functionalized graphene field-effect transistors

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Dopamine is a neurotransmitter with critical roles in the human brain and body, and its dysfunction underlies brain disorders such as Parkinson's Disease and schizophrenia. However, current sensors to detect dopamine in the brain lack relevant selectivity or sensitivity hindering the development of reliable diagnostics and the potentiation of earlier and more efficient treatment. Our previous work reported electrolyte-gate graphene transistors for DNA detection down to the attomolar level [1] using DNA functionalization and protein detection on a picomolar range [3] using antibody functionalization. In this work, we adapted this technology to detect dopamine by using a dopamine-specific aptamer for high selectivity and specificity [2]. The aptamer was immobilized onto a graphene field-effect transistor's channel by a previously reported functionalization process with a pyrene derivate linker [3]. The sensor signal is the charge neutrality point, V_{Dirac} , in the transistor transfer curve. Dopamine detection experiments were performed using phosphate buffered-saline solution (PBS 1x) and artificial cerebrospinal fluid (aCSF) as the electrolyte gate solution. Dopamine was diluted in these solutions from 0.1 pM to 1 aM. Figure 1 (left) shows the linear transistor response to dopamine, diluted in PBS 1x, from attomolar level to 0.01 picomolar concentration followed by saturation at 0.1 picomolar, with 10mV/dec sensitivity. Figure 1 (right) shows selective dopamine detection compared with transistor's response to L-Dopa, L-Tyrosine, Homovanillic acid and, L-Ascorbic acid. These results show that the combination of graphene field-effect transistors with a dopamine-specific aptamer allows highly selective and sensitive dopamine detection. The measured detection limit is the lowest ever reported for dopamine. These promising results allow us to consider further experiments in an *in vivo* setting.

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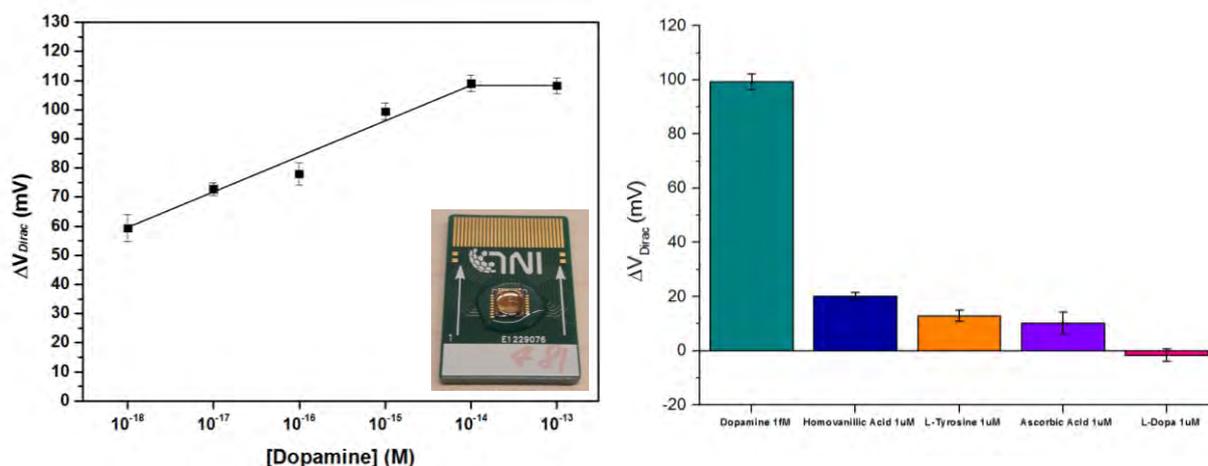


Figure 1: Calibration curve obtained measuring the Dirac point of 20 graphene EGFETs by applying a V_{DS} of 1mV and sweeping V_{GS} from 0V to 1V (left); a graphene EGFET chip is shown in the inset, and the sensors' response compared to non-specific targets, being all diluted in PBS 1x (right).

Design and fabrication of surface relief diffractive optical elements

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Surface relief diffractive optical elements (DOE) are flat devices that modulate the phase of the incoming wavefront by locally altering the optical path. DOE applications have evolved greatly from spectroscopy and diffractive lenses [1], to holography, beam shaping [2] and more recently augmented reality [3]. Iterative Fourier transform algorithms (IFTA) have facilitated the design of DOEs to produce any arbitrary computer-generated intensity pattern [4]. However, the complexity in the design and fabrication increases dramatically as larger diffraction angles are desired, requiring higher pixel resolution, and precise multilevel depth control to optimize diffraction efficiency, and considering distortions in the modelling [5]. Here we present the ongoing development of an IFTA-based design tool to generate arbitrary DOE phase masks, considering microfabrication constraints. Microfabricated transmissive surface relief ($\Delta z \approx 1 \mu\text{m}$) binary DOEs were demonstrated on a glass substrate for $1 \mu\text{m}$ to $5 \mu\text{m}$ pixel resolutions and evaluated using a green laser source. The phase mask was defined with direct write laser on photoresist, followed by SiO₂ glass substrate etching. The binary phase mask results in a mirrored replica of the pattern around the zero order, and geometrical distortions are observed for higher diffraction orders. The zero order is accentuated due to the mismatch of the topography depth from the expected π -phase. DOEs with multilevel phase topography enable not only higher diffraction efficiency, reducing the zero order, but also elimination of the mirrored image. These optical devices may be mass replicated using nanoimprint or embossing techniques onto polymeric substrates or coatings, significantly reducing production costs. For high power applications, such as to increase throughput of laser structuring and texturing, the DOEs may be etched onto fused silica glass for improved thermal stability and robustness. These preliminary results validate the design and fabrication process of custom DOEs. Future work consists in introducing distortion compensation for large diffraction angles in the design tool, and non-binary DOE microfabrication and replication.

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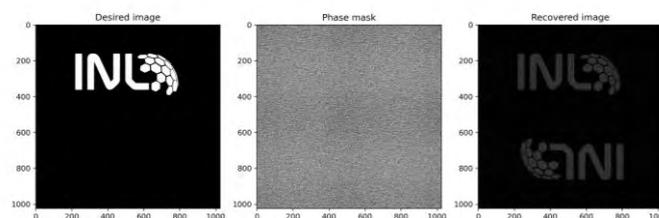


Figure 1: Results of the DOE design tool used to generate binary and multilevel phase masks and evaluate the expected projected pattern intensity.

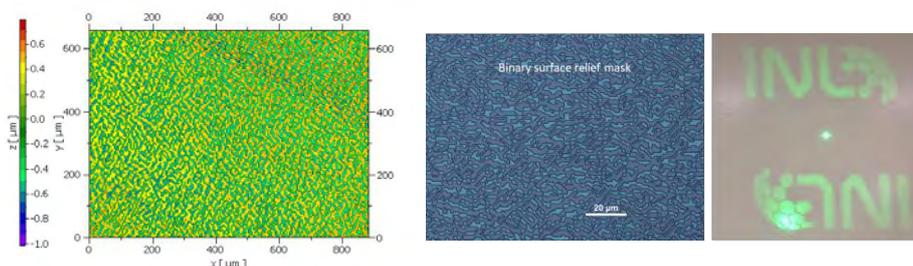


Figure 2: Experimental (left) topography and (middle) microscope measurements of binary DOE devices and (right) projected pattern on a white screen using a green laser source.

Milk exosomes as natural curcumin nanocarriers in liver fibrosis

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Introduction: Exosomes are natural extracellular nanovesicles involved in cell-cell communication. These natural nanovesicles are currently emerging as alternative platform against synthetic nanoparticles. Their nanometric size and lipidic structure, similar to liposomes, allow the incorporation of hydrophilic and hydrophobic drugs in their structure for their controlled delivery in desirable tissue [1, 2]. Hydrophobic drugs such as curcumin present limitations as low bioavailability and solubility. These limitations can be overcome using milk exosomes as nanocarriers of targeted therapy improving their bioavailability and keeping their anti-inflammatory activity [3, 4].

Materials: An active cargo method employing saponin was optimized for the incorporation of curcumin in the exosome structure. Curcumin (1000 µg), saponin (2 mg) and milk derivative exosomes (200 µg) were mixed at 37°C for 20' and purified by size exclusion columns (ExoCur). Physicochemical characterization of ExoCur was carried out by nanodrop, nanophotometry and flow cytometry (FC) for cargo and delivery analysis and by NTA, DLS and TEM for morphology. Cellular assessment of ExoCur cytotoxicity and uptake were performed by MTT assay in RAW264.7 and HepG2 cells. FC and confocal microscopy were used to assess the *in vitro* uptake of the nanoconjugate. *In vivo* evaluation of the therapeutic effect of ExoCur was performed in hepatic model of acute chronic liver disease, produced by CCl₄ agent. Mice treated with CCl₄ received 3 injections of ExoCur (30 µg, 100 µL PBS) or corn oil (control).

Results: Our active approach employing detergent (saponin) allowed curcumin incorporation in goat's milk exosomes structure. Fluorescence properties of curcumin confirmed the presence of the drug in the exosome structure with a cargo of 3.6 µg of curcumin/µg exosome. No membrane and size modification were confirmed by NTA, DLS and TEM (ExoCur: 120±6.1 nm). The controlled release of the curcumin from ExoCur was confirmed by absorbance, measuring a maximal curcumin delivery of 44.7% after 48 h of incubation. Cytotoxic activity of ExoCur was confirmed in both cells in a dose and time- dependent effect, with higher cytotoxicity in macrophages (% viability, RAW264.7: 18.6% and HEPG2: 36.1%). Preliminary *in vivo* results confirmed therapeutic effect of ExoCur, showing a reduction of the fibrotic tissue in chronic liver model.

Conclusions: We have developed the novel nanometric drug delivery system ExoCur based on the encapsulation of the therapeutic molecule curcumin in the structure of nanometric milk exosomes. The novel nanocarrier ExoCur confirmed a therapeutic effect on targeted hepatic tissue, showing a reduction of fibrotic tissue in CCl₄ treated-mice.

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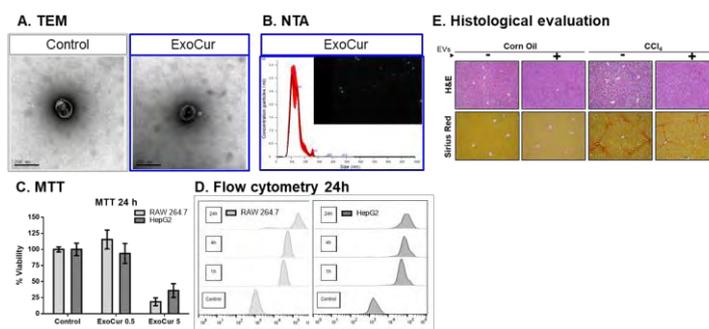


Figure 1: (A)-(B). Physicochemical characterization. (C)-(D) *In vitro* evaluation in cell lines. (E) *In vivo* assessment in CCl₄-treated mice.

Development of a magnetron sputtering deposition process for $\text{In}_2\text{O}_3\text{:H}$ transparent back contact for $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based solar cells

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Abstract

Semi-transparent photovoltaic technologies combine the benefits of visible light transparency and light-to-electricity conversion [1], which can be integrated into windows to be used in buildings. Thin-film $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) solar cells have high conversion efficiency (23.35% ([2])), direct bandgap, high absorption coefficient, low temperature coefficient and less material waste [3], [4], becoming an interesting candidate for this type of application. CIGS solar cells commonly use Mo as back contact. Therefore, to use a transparent conductive oxide, such as $\text{In}_2\text{O}_3\text{:H}$ (IOH), some requirements are needed, such as (1) create an ohmic contact to the absorber, (2) be highly transparent and, (3) exhibit a low sheet resistance [5]. In this work, a deposition process where oxygen was pulsed during the entire deposition process was investigated. To optimize the optoelectronic properties, the sputtering conditions were varied including RF power, O_2 pulse and flow, Ar/H_2 flow and duration. The pulse variation consisted in providing oxygen for one minute in intervals varying from 2, 3 to 4 minutes. After deposition, the films were post-annealed in vacuum at 200 °C for 1 hour. The IOH film electrical properties were characterized by 4-point probe, and the optical properties by transmittance measurements. The oxygen plays an important role in optoelectronic properties, where a high content of oxygen allows higher transparency but also increases the sheet resistance. The best balance between electrical and optical properties of IOH was obtained for a RF power of 30 W, total gas pressure of 6.4×10^{-3} mbar, duration of 180 minutes, with pulses of two minutes without oxygen and one minute with oxygen, resulting in an IOH film with a thickness of approximately 420 nm, average visible transparency over 80% and sheet resistance before and after annealing of 23 and 17 ohms/sq, respectively.

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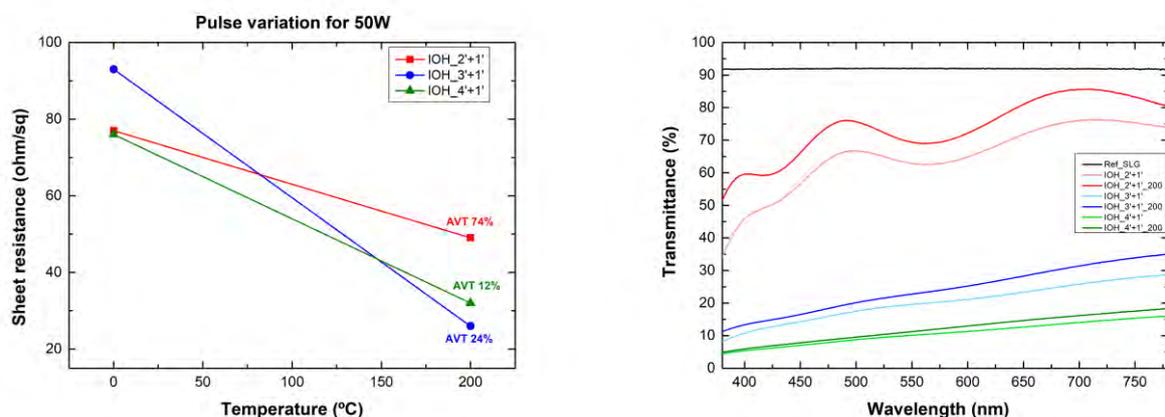


Figure 1: Sheet resistance and transmittance of samples deposited with different pulses at 50W, with an O_2 and Ar/H_2 flow of 1.5 sccm and 2 sccm, respectively. Thickness of the film ~345 nm.

Photo-induced functionalization of gold nanorods for biosensing of proteins

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Gold nanoparticles of elongated shape, such as gold nanorods, display longitudinal surface plasmon (LSP) resonances that are very sensitive to the refraction index close to the particle's surface. One type of biosensors that exploits this feature for optical detection of biomolecules are plasmonic biosensors.^[1] But commonly, the particle's sensitivity is not homogeneously distributed across the surface, instead it is concentrated at regions of large plasmon-enhanced near-field, known as hot-spots. An example of plasmon hot-spots are the tips of gold nanorods. Thus, tip-selective functionalization of these hot-spots with bioreceptors is crucial to develop plasmonic biosensors with improved response by capturing the target species at the most sensitive regions of the particle.^[2] In this contribution, we show a novel strategy that aims at tip-selective functionalization of gold nanorods implemented in a model plasmonic biosensor. For this purpose, we use a photocrosslinking reaction to attach biotin receptors onto gold nanorods immobilized on a glass surface (Figure 1A). The photochemical reaction is performed by irradiation at the LSP's wavelength in order to trigger photo-conversion at the plasmon-enhanced near-field regions, thus imparting spatial selection of hot-spots. The irradiated samples show improved responses to the protein streptavidin compared to non-irradiated control samples, as expected for biotin-functionalized particles (Figure 1B). The dose-response curve shows that the LSP peak position red-shifts as protein concentration increases in the nanomolar range and it saturates at a peak shift of ca. 4 nm (Figure 1C). This approach can be generalized to any anisotropic particle shape and to any other type of bioreceptor, e.g. antibody, aptamer or other nucleic acid, being thus important for the development of innovative and more sensitive biosensors, for example for medical diagnostics.

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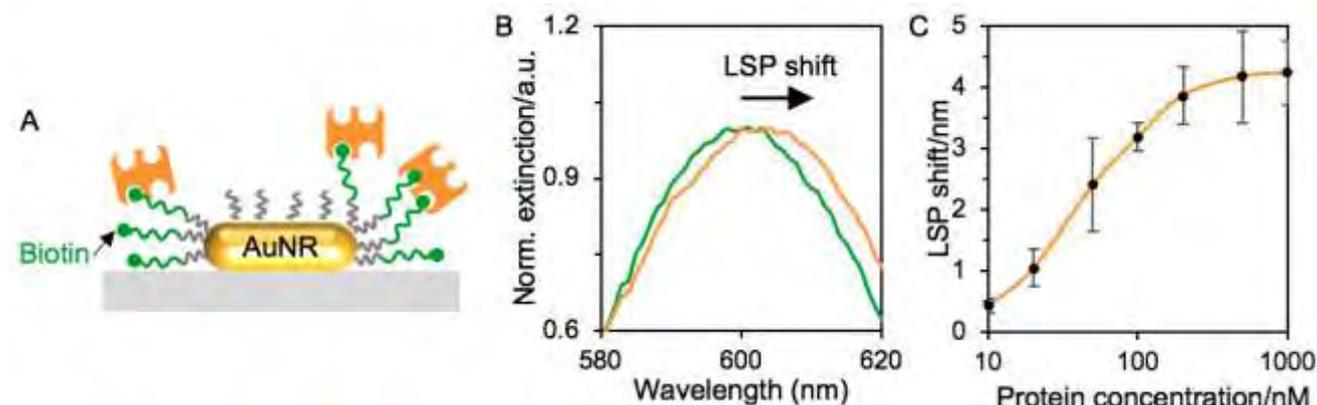


Figure 1: Biosensing of streptavidin protein using photo-induced tip-functionalized gold nanorods. (A) Model plasmonic biosensor. Gold nanorods are tip-functionalized with a biotin-derivatized photocrosslinker (green) and then used for sensing streptavidin (orange). (B) Streptavidin causes a change in the refraction index around the gold nanorod, which is detected by a shift in the LSP peak of the particle. (C) Dose-response curve for streptavidin showing a high LSP shift of around 4 nm for the higher concentration of protein.

Redox responsive manganese-based MRI theranostics for cancer therapy

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Smart theranostics are dynamic platforms that integrate multiple functions, including at least imaging, therapy and responsiveness, in a single agent. [1, 2]. This work focuses on the synthesis, characterisation and evaluation of manganese dioxide (MnO₂)-based redox responsive magnetic resonance (MR) nanotheranostics for cancer therapy. These systems feature a Pt(IV) complex as a chemotherapy prodrug, bound to MnO₂ nanoparticles. In the presence of reducing agents (e.g. glutathione), the Pt(IV) complex is reduced, thus releasing the active drug cisplatin. The same agents also reduce the MnO₂ particles to Mn(II), inducing an OFF-ON T₁ MR signal switch (Figure 1A).

Using facile ultrasonication reactions [3], we investigated a series of Mn_xO_y-Pt(IV) samples in regards to their performance as redox-responsive MR contrast agents. Relaxometry studies performed at 1.47 T revealed signal enhancements as high as 136-fold for nanoparticles with lower Pt/Mn ratios after treatment with a reducing agent, in agreement with the MRI contrast enhancement observed in phantom images acquired at clinical fields of 3T (Figure 1B). Cell cytotoxicity was also assessed in a lung carcinoma (A549) cell line in order to study the therapeutic effect of the developed conjugates (Figure 1C). Results in 2D cultured cells show a lower toxicity for the MnO₂-Pt(IV) nanosystem (IC₅₀ = 100.0 μM) when compared to that of cisplatin (IC₅₀ = 31.6 μM), but considerably higher toxicity than that of a Pt(IV) prodrug (IC₅₀ = 420.5 μM). This highlights a dual therapeutic effect where the Mn(II) species play a key role. Further cell studies point to the participation of the free Mn(II) ions released from the nanoparticles in Fenton-like reactions, leading to the activation of ferroptosis in addition to apoptosis (by cisplatin). Ongoing *in vitro* studies in 3D A549 cell cultures aim to explore the imaging and therapeutic efficiency of these MnO₂-Pt(IV) nanoparticles in a more representative tumour microenvironment.

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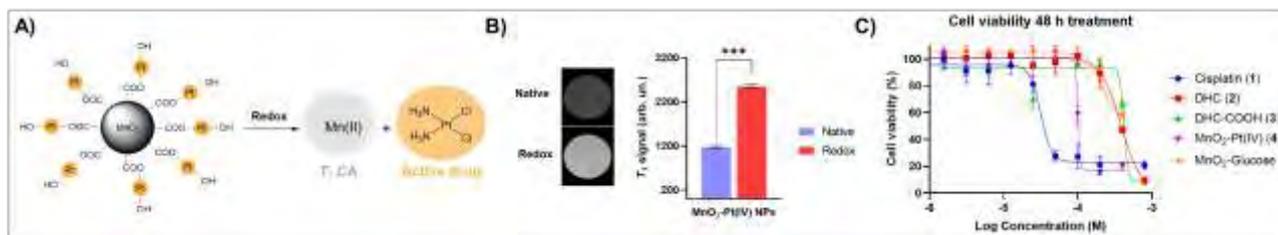


Figure 1: A) Schematic representation of the reduction MnO₂ nanoparticles by reducing agents. B) T₁-weighted MRI phantom images for MnO₂-Pt(IV) nanoparticles and corresponding signal shift with addition of AA (10 mM), [Mn] = 0.2 mM, ***p<0.0001. C) Cell viability of A549 cells after 48 h of treatments (n=3). Concentration refers to Pt concentration for all treatments except for MnO₂-Glucose, in which the Mn concentration is presented.

Ultra-transparent broadband terahertz polarizers by nanoimprint lithography

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The far-infrared (FIR) and particularly the terahertz (THz) region of the electromagnetic spectrum were often described as the final unexplored region of the electromagnetic wave spectrum [1]. This technology's primary applications include imaging in astronomy, spectroscopic techniques, detection of chemicals or explosives, security screening, wide-broadband wireless data communication, dry food inspection, etc. [2]. Thus recently, many functional devices are being developed, such as THz emitters, detectors, and passive components, e.g. lenses, filters, attenuators, and polarizers. In particular, polarizers are essential tools in spectroscopy. These devices manipulate the polarization degree of freedom of THz electromagnetic waves. Principally, linear polarizers are designed to separate light into two perpendicular polarization directions [3]. The linearly polarized component is transmitted, and the other component is either reflected or absorbed.

We report the largest broadband terahertz (THz) polarizer based on a flexible ultra-transparent cyclic olefin copolymer (COC) film. The COC polarizers were fabricated by nanoimprint soft lithography with the lowest reported pitch of 2 or 3 μm and depth of 2 or 3 μm and sub-wavelength Au double wire grid polarizer (DWGP) configuration. Fourier-Transform Infrared spectroscopy was used in a broad range of 0.9 - 20 THz to show transmittance of the bulk materials and fabricated polarizers based on Si and polymers. COC polarizers present superior performance than Si polarizers, with extinctions ratios of at least 4.4 dB higher, more than doubled transmission intensity, and a larger operating band. Numerical simulations support results from polarizer characterization. Both Si and COC polarizers fabricated in this work show a wider operation band than a commercial polarizer. Fabrication of the polymer polarizers can be easily up-scaled, indeed meeting functional requirements for many THz devices and applications, such as high transparency, lower-cost fabrication, and made of durable and flexible material.

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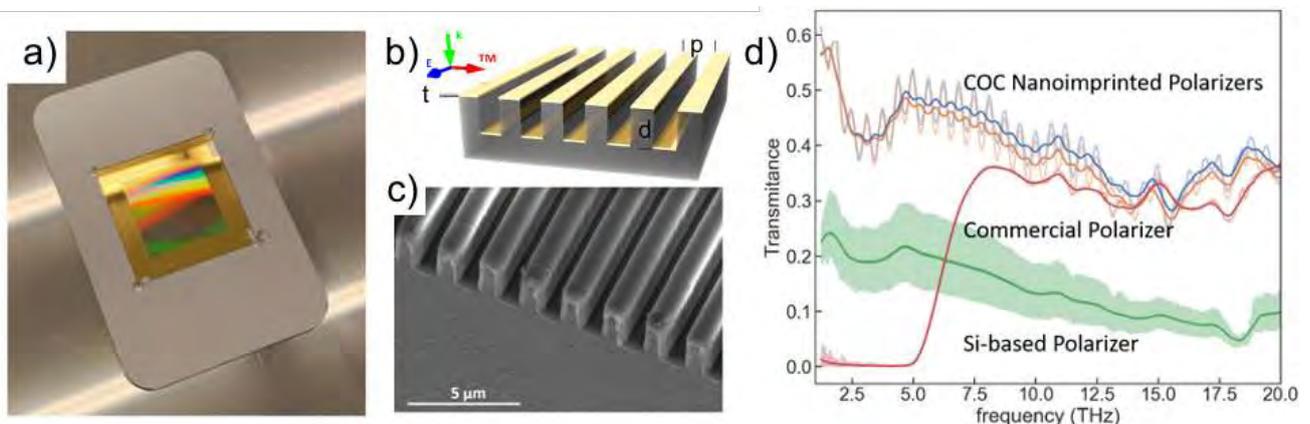


Figure 1: a) COC DWGP in the alignment support. b) Schematic sideview of double wire grid polarizer in COC/Si (grey) and gold (yellow). c) Cross section SEM image of COC DWGP. d) Transmitted intensity of single polarizers with $t = 0.1 \mu\text{m}$: A) COC $p = 2 \mu\text{m}$, $d = 3 \mu\text{m}$ (blue), B) COC $p = 3 \mu\text{m}$, $d = 3 \mu\text{m}$ (orange), C) Si $p = 1 \mu\text{m}$, $d = 2 \mu\text{m}$ (green), and, D) commercial F350 polarizer from Bruker (red).

Self-reporting Nanoparticles for Cancer Immunotherapy

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The tumor microenvironment (TME) is composed of infiltrating immune cells that can dictate the progression of the primary tumor. Usually, the immune response is suppressed in the TME but with the aid of immunostimulating (IS) drugs, the immune system can be reprogrammed to fight cancer. Current cancer therapies are often non-specific, inefficient and result in severe side effects. Taking advantage of the characteristics of the TME and nanotechnology, we have designed magnetic pNIPAM nanocarriers that respond to temperature (T) (induced by magnetic hyperthermia) in order to release a cocktail of IS drugs in the TME, resulting in a targeted, more specific cancer therapy. Temperature-responsive magnetic pNIPAM nanoparticles of 250nm in size were synthesized through wet chemistry approach. An IS drug was efficiently encapsulated into the polymeric shell and the final pNIPAM formulations were characterized using spectroscopic techniques, TEM, and magnetometry. The responsiveness of the pNIPAM nanoparticles to changes in temperature was confirmed via UV-Vis. Cell-mediated cytotoxicity assays were established to test the capacity of the nanocarriers to promote tumor cell death. We co-cultured HT-29 cells (colorectal cancer cell line) with NK92CI cells (NK cell line) at different ratios and in the presence of IS drug. The viability of the tumor cells was measured using a fluorescence redox indicator for cell viability. Initial results show that free IS drug and unloaded pNIPAM have no direct effect on the cell viability of immune cells or tumor cells, but in the cell-mediated cytotoxicity assay, the tumor cell killing is enhanced when NK cells are stimulated with IS drugs. The final formulation (pNIPAM-IS drug) induced NK cell activation and tumor cell killing, which was enhanced after magnetic hyperthermia. Future work includes the synthesis and characterization of a self-reporting probe activated by immune cells. The final goal is to develop a new and efficient nanoparticle-based system to be applied in colorectal cancer theranostics.

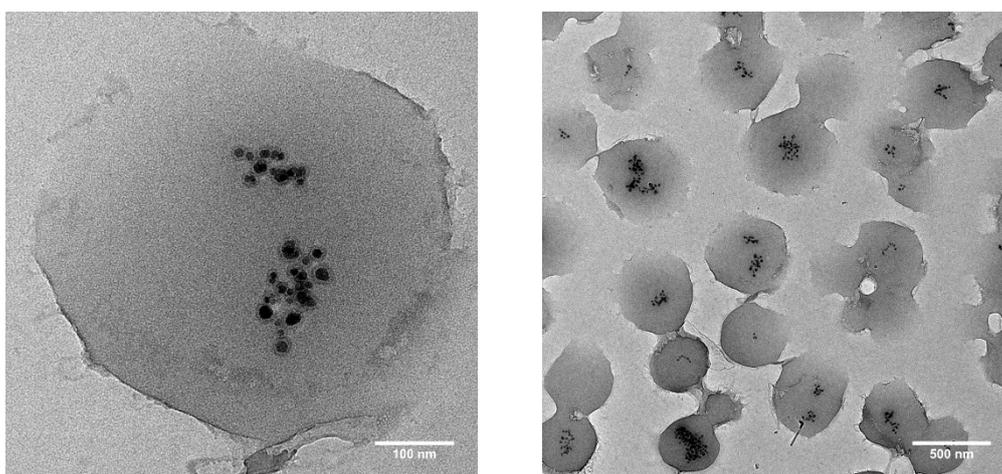


Figure 1: Image of the pNIPAM nanoparticles by transmission electron microscopy

Receptor surface decoration improves the anticancer activity of cannabinoid-loaded nanoparticles through delayed cell internalization

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Δ^9 -tetrahydrocannabinol (Δ^9 -THC) is known for its antitumor activity and palliative effects [1, 2]. However, its unfavorable physicochemical and biopharmaceutical properties, including psychotropic side effects due to unspecific biodistribution and resistance mechanisms associated to dosing, make mandatory the development of successful drug delivery systems [1, 2]. Hence, our team previously developed Δ^9 -THC-loaded poly(lactide-co-glycolic) nanoparticles (THC-PLGA NPs) [3]. Subsequently, Tf surface-modified THC-PLGA NPs (Tf-THC-PLGA NPs) were designed and evaluated as a novel THC-based anticancer therapy with the aim of optimizing the interaction of THC-PLGA NPs with cancer cells. In addition, to assess the interaction and expected fate of both the nanocarrier and the loaded drug following exposure to the cells, a double-fluorescent strategy was applied, consisting of both the chemical conjugation of a dye to the nanoparticle polymer and the encapsulation of either a lipophilic or a hydrophilic dye. The interaction of the resulting nanocarriers with Caco-2 cells, a cancer cell model bearing both cannabinoid and transferrin receptors, was evaluated. Upon incubation with the cells, both plain THC PLGA NPs and Tf-THC PLGA NPs avoided moderate cell viability increases exerted by free THC at short incubation times, which have been associated in the literature to drug resistance mechanisms. Furthermore, Tf-THC PLGA NPs exerted higher and faster cancer cell death compared to plain nanoparticles (cell viability decrease down to 17% vs. 88). However, their internalization was significantly slower than plain nanoparticles. Uptake studies in the presence of inhibitors indicated that the nanoparticles were internalized through cholesterol-associated and clathrin-mediated mechanisms. Overall, the observations suggested that the improved Δ^9 -THC antitumor effect was potentially due to increasing the presence of the nanocarriers, and hence maximizing the amount of drug locally released, at the surface of cells bearing cannabinoid receptors, instead of improving internalization. The results obtained highlight the promising potential of Δ^9 -THC-loaded nanocarrier-based antitumor therapies, as well as exploring further strategies aimed at modulating the nanocarrier action at the cell surface.

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Shear-collapsible microscale aggregates of PLGA nanoparticles with the ability to target obstructed blood vessels

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BACKGROUND

Obstruction of critical blood vessels as in thrombosis and atherosclerosis is a leading cause of death and long-term adult disability worldwide. Effective treatment requires quick and invasive interventions through the systematic infusion of thrombolytic agents or the placement of a catheter in the affected vessel. Moreover, non-selective distribution of the thrombolytic drug increases bleeding risk. Blood vessels with luminal stenosis (narrowing) show a significant increase in fluid shear stress (>1000 dyne/cm²) compared to normal vessels (~70 dyne/cm²), a fact that can be exploited for targeting delivery to obstructed vessels.

OBJECTIVE

To prepare microscale aggregates of PLGA NPs with the ability to breakup under high shear stress into their forming NPs, which in turn adhere more effectively to the vessel surface compared with larger aggregates.

METHODS

Negatively and positively charged NPs were prepared based on poly(ethylene glycol) (PLGA) using an emulsion-solvent evaporation method. Nanoparticles surface charge was modulated by using carboxylic or amine species. Next, the microaggregates were prepared by mixing the negatively and positively charged NPs using a high-speed homogenizer. Optimized aggregates were achieved by controlling different parameters as: (i) composition of NPs; (ii) NPs ratio; or (iii) homogenization conditions (speed, duration). The produced NPs and aggregates were extensively characterized. To test the ability of the microaggregates to collapse under high shear stress, they were injected through a microchannel specially designed to mimics different vascular grading stenosis (low, medium, high). Furthermore, HUVEC cells were cultivated in the microfluidic system and labelled aggregates (Nile red-negative NPs and (FITC-positive NPs) were injected into the microchannel and observed under fluorescence microscope.

RESULTS

Particle size and zeta potential were 268.5 nm, -20.1mV and 179.2 nm, +20.9 mV for negative and positive NPs, respectively. The microaggregates had a globular shape and an average diameter of 6.8 µm. Aggregates passed through the microchannel contained ~30% of NPs as a result of aggregates collapse under the elevated shear. In addition, examination under fluorescence microscope provided another evidence for aggregates breakup.

CONCLUSION

The PLGA-based microaggregates show promise for targeted treatment of thrombosis, arteriosclerosis and thrombosis-associated disorders such as COVID 19 infection.

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FIGURES

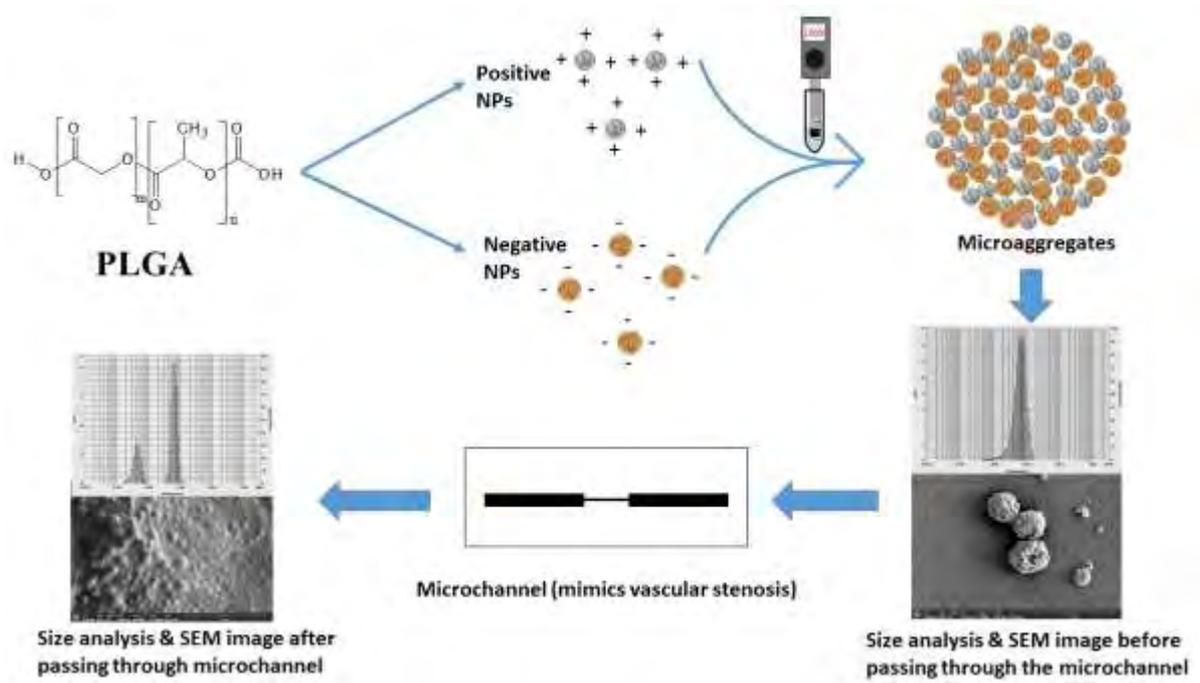


Figure 1: Synthesis of microscale aggregates with the ability to break up under high shear stress.

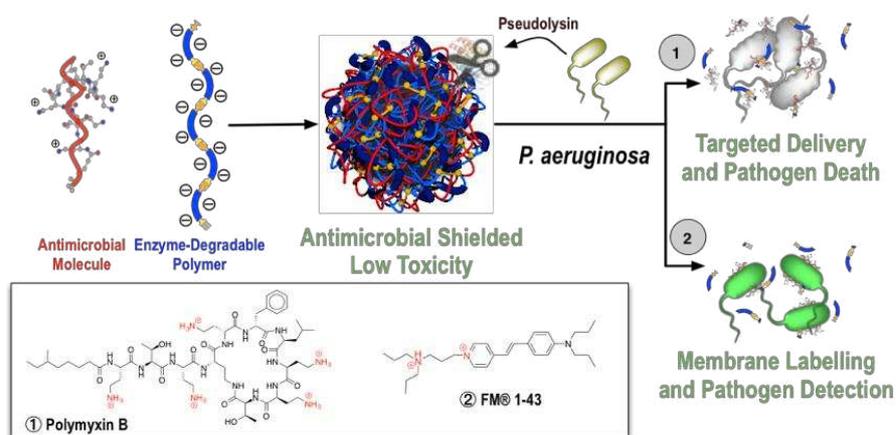
Enzyme-Degradable Polyion-Complex (PIC) Particles for the delivery of antimicrobial peptide polymyxin B.

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PIC particles are stabilised by these electrostatic interactions between its components, and thus are especially suited for the delivery of charged (bio)molecules (e.g. nucleic acids and proteins), which are prevalent in nature. This way, delivery vehicles can be formulated without the need to introduce chemical modifications to these (bio)molecules and as a result the biological activity of these molecules should be maintained upon release. Here, we describe novel polyion complex (PIC) particles for the delivery of Polymyxin B (*Pol-B*), an antimicrobial peptide currently used in the clinic as a last resort antibiotic against multidrug-resistant gram-negative bacteria. Towards this end, we have prepared polymer containing peptide sequence (-Glu-Gly-Leu-Ala-) this sequence is selectively degraded by *pseudolysin*, an elastase produced by opportunistic pathogen *Pseudomonas aeruginosa*.¹ A range of conditions for the controlled assembly of Pol-B with polymer containing peptides has been identified which let us prepare stable colloidal PIC particles containing different Pol-B:Polymer ratios. Their stability under simulated physiological conditions (*i.e.* pH, osmotic pressure and temperature) characterised. Furthermore, preliminary evaluation of the antimicrobial activity of these Pol-B containing PIC particles has been performed, by monitoring their effect on the growth of *Pseudomonas aeruginosa*, an opportunistic gram-negative bacterium.



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Improved Gold Nanoparticle Probes for Molecular Detection of Metabolic Diseases

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There is an overall increase in life expectancy associated to high costs in health care for an ageing population in the industrialized world. Consequently, there is a demand for fast, unexpensive and easy to use diagnostic tests that are essential in identifying patients, determining prognosis, monitoring treatment and assessing the efficacy of prevention. [1] Here, nanotechnology has a prominent role, with special emphasis on gold nanoparticles (AuNP) for detection of Single Nucleotide Polymorphisms (SNP) associated with metabolic diseases with high prevalence, such as lactose intolerance. [2, 3]

The aim of the current project is (i) to synthesize and characterize spherical-AuNPs with different diameters; (ii) to functionalise AuNPs with specific oligonucleotide in order to obtain stable Au nanoprobe; (iii) development and optimization of a nanotechnology-based colorimetric assay for detection of an SNP related to lactose intolerance (LCT13910C>T) (Figure 1).

Spherical AuNPs with two distinct diameters (15 and 40 nm) were successfully synthesized, based on a citrate-reduction method and further characterized by Ultraviolet-visible spectrophotometry, Dynamic Light Scattering (DLS), Electrophoretic Light Scattering (ELS) and Nanoparticle Tracking Analysis (NTA). Their functionalization was further performed based on either a salt ageing or a pH method, using a thiol-modified oligonucleotides (5'-(SH-C₆)-AGTTCCTTTGAGGCCAGGG-3'). The pH method allowed Au nanoprobe with improved colloidal stability, and using less oligonucleotides for full capping, in comparison with the more widely used Salt ageing functionalization method. In the colorimetric assays, when nanoprobe were incubated with target DNA and upon salt induced aggregation, the colour of nanoprobe visibly changes from red (negative) to blue (positive) depending on the type of DNA present (Complementary = lactose intolerance, Mismatch = lactose tolerance or Noncomplementary). In conclusion, we successfully establish an innovative, faster, and simpler colorimetric molecular assay for SNP detection associated to lactose intolerance. The validated assay using synthetic DNA target and PCR products from sample patients will be considered for prototype at STABVida, and apply for detection of other single nucleotide polymorphisms related to metabolic and genetic diseases.

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FIGURES

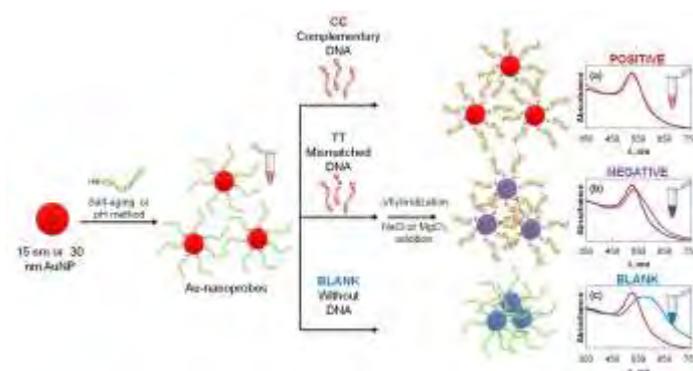


Figure 1: Scheme of the proposed colorimetric assay for SNP detection.

Few-layer hexagonal boron nitride production for high technology

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Two-dimensional (2D) materials are a topic of high interest in the materials science community for the engineering of novel devices. 2D hexagonal boron nitride (hBN), an insulator with lattice structure similar to graphene, is seen as an optimal candidate for several electronic applications, in particular in photonics and optoelectronics [1]. Interestingly, highly stable and bright single photon emission (SPE) at room temperature was observed in thin hBN samples, most likely due to the excitation of defects in the crystalline lattice [2]. Despite a considerable effort, a method that would guarantee a large-scale, high-quality and low-cost production of this material is still needed. Among the several methods available, chemical vapor deposition (CVD) appears as one of the most controllable, systematic and reliable. CVD affords the possibility of fine tuning the process parameters to achieve high-quality hBN, in compliance with the prospective demand of industrial technology. In this work, we report the growth of large-area, uniform and pristine few-layer hBN by using atmospheric-pressure CVD (AP-CVD). Although the use of low pressure is usually associated to hBN samples with higher quality and improved uniformity [3], we were able to achieve a comparable sample quality by a simpler approach. hBN films were grown on Cu foils and then transferred to different substrates for extensive characterization by a wide range of techniques. A simple and up-scalable production method for hBN might soon unlock the potential of this material for the fabrication of SPE devices for quantum information processing [4].

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FIGURES

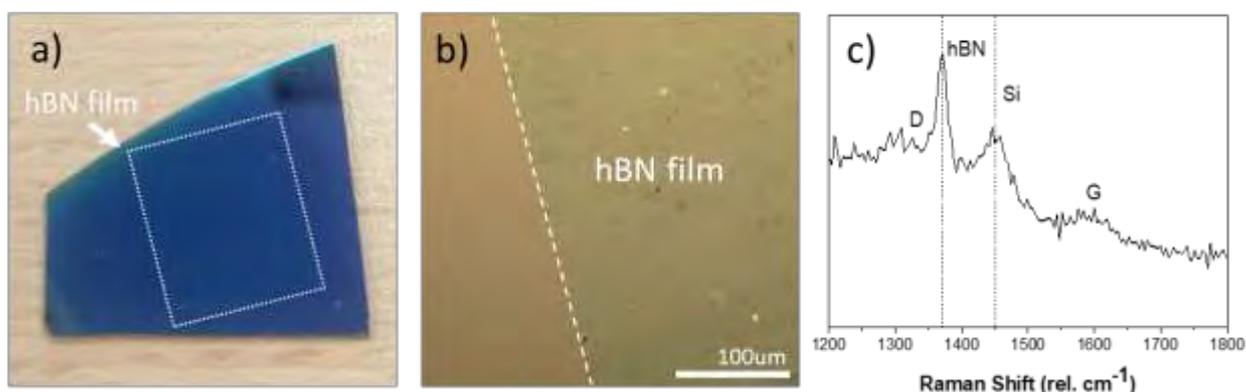


Figure 1: a) Photograph of the transferred hBN film on a Si/SiO₂ substrate. b) Optical microscopy image of the hBN film edge on a Si/SiO₂ substrate. c) Raman spectrum of the hBN film.

Graphene Magnetic Nanoparticles as multifunctional smart drug delivery nanosystems for cancer theranostics

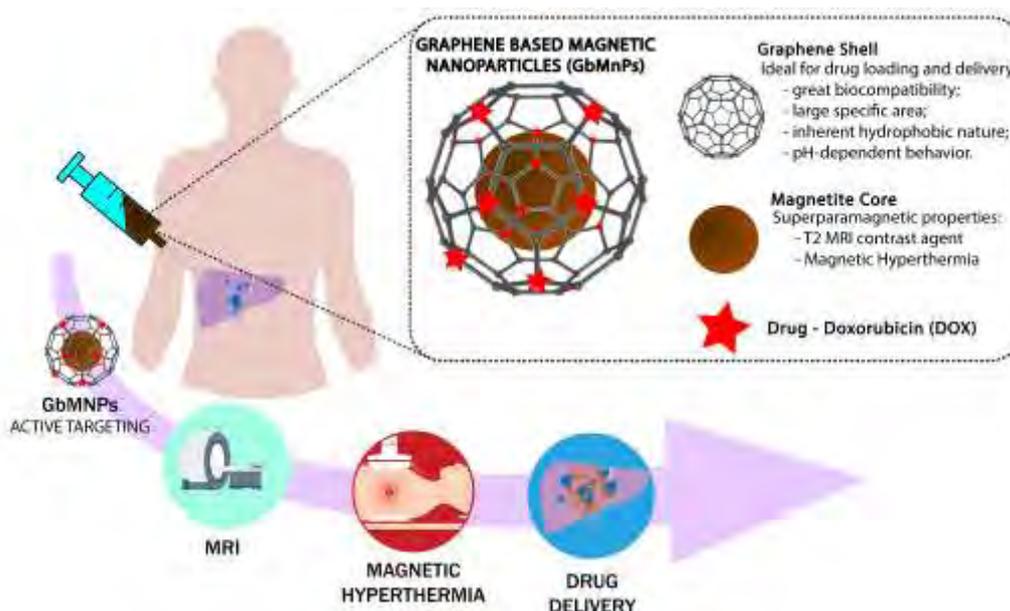
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The purpose of this study was to validate the theranostic performance of graphene-based magnetic nanoparticles (GbMNPs) against tumoral hepatic cell lines. In the GbMNPs, the core nanoparticle made of magnetic material is located in the hollow cavity enclosed by an outer carbonaceous shell. The unique properties of GbMNPs combine physicochemical properties from both graphene and iron oxide (Fe₃O₄) counterparts, such as biocompatibility and non-toxicity, superparamagnetic behaviour with high saturation magnetization, and high drug encapsulation efficiency and loading capacity provided by the hydrophobic interactions between the certain drug molecules and the particular bidimensional structure of graphene. The in vitro tests revealed the ability of GbMNPs in combining magnetic resonance imaging (MRI) with therapy, exhibiting (i) a r_2 relaxivity value of $\sim 364 \text{ mM}^{-1}\text{s}^{-1}$, (ii) a high heating efficiency under an alternating (AC) magnetic field – magnetic hyperthermia – (independent loss power of $1.83 \text{ nHm}^2 \text{ kg}^{-1}$) and (iii) a drug (doxorubicin, DOX) loading efficiency of 96% with a pH- and temperature-dependent release. Cytotoxicity studies with HepG2 cell line showed that the cell viability was reduced to 36% when tested with DOX-loaded GbMNPs (GbMNP@DOX) under an AC magnetic field. In order to study the nanoparticles cellular internalisation, cells were incubated with increasing concentrations of GbMNPs for 24h and imaged by MRI. A concentration-dependent T₂-MRI contrast enhancement was observed, as denoted by the remarkable decrease in the T₂ relaxation time as Fe concentration increases. Additionally, a 3D liver cancer organoid was bioengineered as a more representative human model of disease to in vitro validate the therapeutic performance of GbMNP@DOX. Cell viability studies performed in the liver tumoroid over time indicated that it remained viable beyond the 2 weeks mark, showing an enhanced functional activity when compared to 2D cultured cells, as denoted by an increase in the transferrin and albumin production levels of 46% and 86%, respectively. In order to assess the therapeutic performance of GbMNP@DOX in a relevant model of disease, a functional validation was performed against the developed 3D liver cancer organoid. Results showed showing a large decrease in cell viability, with 65% of viable cells, which was further reduced to only 2% of viable cells with application



of magnetic hyperthermia.

Figure 1: Schematic representation of the graphene based magnetic nanoparticles as multifunctional smart drug delivery nanosystems for cancer theranostics

Biological behaviour of UCNPs loaded aerogel scaffolds

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Aerogels are the lightest solids on Earth with outstanding physical properties like highly porous, high specific surface areas and low densities [1]. Furthermore, aerogels exhibit tunable mechanical properties, composition and porous structure making them attractive for biomedical applications. Nevertheless, the difficulty to track and monitor them and their degradation products in a non-invasive way after their implantation through an *in vivo* imaging method is still a challenge. In this context, upconversion nanoparticles (UCNPs), also known as “new generation fluorophores”, present unique luminescent properties, deep near infrared light penetration into biological tissues, excellent detection sensitivity and low toxicity [2]. Specifically, rare earth based UCNPs are excellent fluorescent bioimaging labels able to convert infrared light into visible light [3]. For this reason, UCNPs have been employed for *in vitro* and *in vivo* bioimaging and biodetection applications without significant toxicity. In this work, UCNPs were synthesized by a co-precipitation method from rare earth elements followed by a silica coating step. Then, aerogel scaffolds were manufactured and loaded with UCNPs and the success of this incorporation was assessed by microscopy techniques. Finally, UCNPs loaded aerogels were evaluated regarding their *in vitro* biological behavior by cytocompatibility, adhesion and migration tests.

ACKNOWLEDGEMENTS:

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Designing Antibiotics-Free Novel Biomaterials That Combat Bacterial Infections

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Abstract

The novel antimicrobial concept “bacteria starvation therapy” is developed to empower extraction of extracellular electrons from bacterial membrane respiration chain and interruption of energy metabolism of bacteria. The antimicrobial behaviours of large-area graphene film on Cu conductor, Ge semiconductor and SiO₂ insulator show a strong dependence on the band structure of substrate, in the order of graphene-Cu > graphene-Ge > graphene-SiO₂. [1] Moreover, increase of electrical conductivity of graphene-Ge heterojunction by improving graphene crystallinity can enhance the antimicrobial ability. [2] To further verify the antimicrobial correlation with band structure, cobalt doped TiO₂ coatings are designed with tunable bandgap (3.10 eV to 1.55 eV) and the results reveal that narrowing TiO₂ bandgap can remarkably boost the antimicrobial capacity. [3] Recently, through in-situ oxidation of Ti₃C₂T_x MXene, TiO₂-Ti₃C₂T_x heterojunction is fabricated to tailor the band structure (Figure 1). Under light irradiation, the heterojunction can exhibit favourable antibacterial activity. In summary, semiconductor-based materials with tailored band structure are able to act as extracellular electron acceptors, which can disturb the electron transfer and energy metabolism of bacteria, thereby leading to bacteria starvation and death. The “bacteria starvation therapy” can provide new insight into the interactions between bacteria and 2D materials and contribute to the design of novel antimicrobial agents based on 2D nanomaterials.

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FIGURES



Figure 1: SEM images of pristine Ti₃C₂T_x MXene sample (left) and different oxidation degrees of TiO₂-Ti₃C₂T_x heterojunction samples including lightly oxidized O1-Ti₃C₂T_x (middle) and heavily oxidized O2-Ti₃C₂T_x (right).

Efficient Saline Water Electrolysis for Green Hydrogen Production without the Interfering Chlorine Evolution

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Green hydrogen (H_2) produced through water electrolysis in combination with renewable energy sources such as solar and wind has become an important vector of decarbonizing the chemical industry and energy sector [1], which will help to achieve the carbon neutrality goals set out by many countries. For widespread deployment of green H_2 , the cost of water electrolysis must be substantially reduced to make the electrolyzed H_2 competitive relative to that produced by conventional steam reforming. For the commercial alkaline and proton exchange membrane (PEM) electrolyzers currently being deployed, there is generally a stringent requirement for the quality of water fed into the electrolyzer [2]. As a result, ancillary equipment is in most cases needed to desalinate and purify water before it is used for electrolysis. Such desalination/purification units markedly increase the overall cost of the system and thereby the price of H_2 . Therefore, it is highly desirable to develop efficient catalytic materials and membranes as well as to design new electrolyzer configurations to enable direct usage of low-grade or saline water for H_2 production. This is particularly favorable for large-scale offshore H_2 production emerged very recently, taking advantage of the largely abundant and free seawater resources and the capability of installing MW/GW-scale offshore wind and solar farms, as pointed out by the recent techno-economic analyses [3]. However, direct seawater electrolysis faces formidable technological challenges, in particular the chloride evolution reaction (CER) happening at the anode, which competes with the oxygen evolution reaction (OER) and generates unfavorable chlorine and/or hypochlorite that will corrode catalysts, membranes and other components over time and thereby substantially reduce the operation lifetime of the electrolyzer.

In this presentation, we will demonstrate that coupling the cathodic hydrogen evolution reaction (HER) with the hydrazine oxidation reaction (HzOR) taking place at the anode enables the alkaline-saline water electrolysis to occur at a high current density without the unfavorable, interfering CER [4]. Using the bifunctional carbon paper supported Co-Ni-P nanowires (Co-Ni-P/CP) as the cathode and anode (**Figure 1a**), we have accomplished hydrogen production in alkaline-saline-hydrazine electrolyte at 500 mA cm^{-2} with a small cell voltage of only 0.533 V and outstanding stability of 80 hours with minimal degradation (**Figure 1b-d**).

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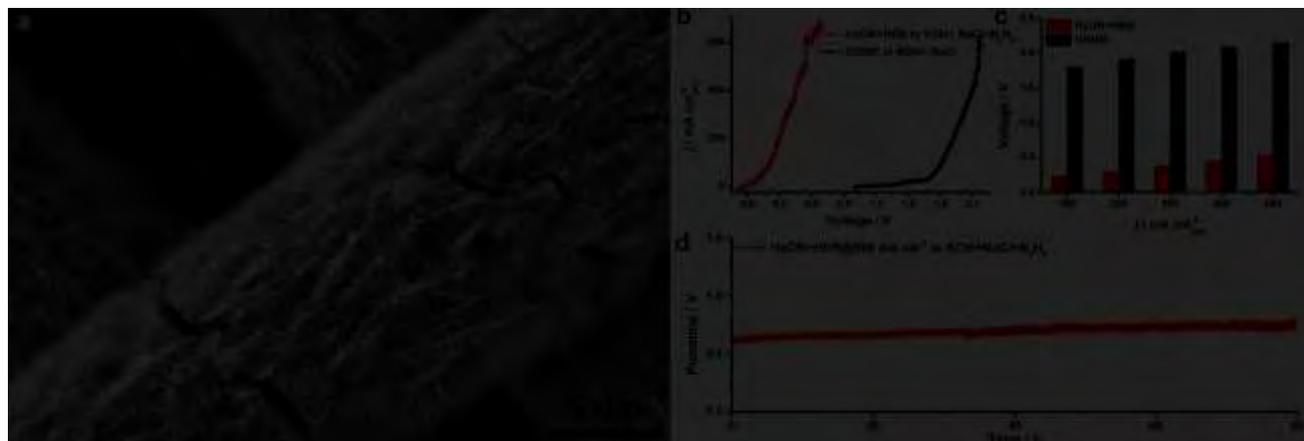


Figure 1: (a) SEM image showing the bifunctional Co-Ni-P NW electrode. (b) LSV curves of the coupled HzOR + HER and overall saline water electrolysis. Scan rate: 5 mV/s. (c) Comparison of cell voltages. (d) Chronopotentiometric curves of the HzOR + HER.

Selective cannabinoid nanoparticles for Atherosclerosis treatment

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Abstract

Atherosclerosis is the major cause of cardiovascular disease death in the developed world, for which there is no specific treatment(1). Currently, the inflammatory process in atherosclerosis is related with the endocannabinoid system. Cannabinoid receptor type 2 (CB2) is expressed in immune cells and is characterized for its anti-inflammatory properties, introducing CB2 agonists as a potential treatment(2,3). Our research group has been exploring a platform of biodegradable, biocompatible and polymeric nanoparticles (NPs) as selective CB2 agonist delivery systems for the treatment of atherosclerosis. For this purpose, we selected JWH-133, a synthetic, selective and potent CB2 agonist. Moreover, since cell adhesion molecule VCAM-1 was highly expressed in the vascular endothelium of the atheroma plaque(4), NPs were functionalized with a VCAM-1 binding peptide (VCAM-1 BP) to target nanosystems in the atherosclerotic region. Polymeric NPs were produced by nanoprecipitation method(5) using a mixture of three types of poly(lactide-co-glycolic): (i) PLGA; (ii) poly(lactide-co-glycolide)-b-poly (ethylene glycol) (PLGA-PEG) and (iii) poly(lactide-co-glycolide)-b-poly (ethylene glycol)-maleimide (PLGA-PEG-Mal) polymers at different ratios. NPs prepared using 85:5:10 w/w ratio of PLGA:PLGA-PEG:PLGA-PEG-Mal, were functionalized with VCAM-1 BP. The NPs were in 150-200nm of diameter, showed spherical morphology, negative surface charge and, high encapsulation efficiency of JWH-133. After conjugation, functionalized NPs maintained their shape and size. Cell viability assays on human umbilical vein endothelial cells (HUVEC) indicated low or non-toxicity for both blank and loaded-JWH-133 NPs. In contrast, cell viability was compromised when free CB2 agonist was incubated at high concentrations, indicating the positive impact of drug nanoencapsulation. Cell NP uptake was studied using fluorescently labeled NPs by confocal microscopy in tumor necrosis factor alpha (TNF α) stimulated cells. TNF α stimulation resulted in a pro-inflammatory profile that mimicked the pathogenic condition. In vitro stimulated HUVEC expressed high levels of VCAM-1, resulting in increased recruitment and cell uptake of functionalised NPs in comparison of non-stimulated cells. These preliminary results highlight the potential of formulated and functionalized NPs loaded with CB2 agonist for the treatment of atherosclerosis.

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Liquid phase exfoliated graphene nanosheets as laminates for water purification

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Graphene and derivatives have drawn increasing attention for their imminent application in various technological fields, such as energy storage and conversion, gas separation and water purification. Over the past decade, graphene oxide and reduced graphene oxide have been explored as membrane materials for water and ion transport systems. However, when these materials are processed into aqueous medium, the produced membranes showed several drawbacks, including swelling, poor mechanical strength and stability issues. Here we describe an approach for the low-cost and large-scale production of graphene nanosheets (GNs) without any oxygen content, suitable to fabricate membrane for water purification. GNs were produced in a non-aqueous and non-toxic solvent (cyrene) via high-shear liquid phase exfoliation (LPE). The GN concentration, measured by thermogravimetric analysis, was as high as ~1 mg/mL. The prepared GN dispersion appeared highly stable over a long period (30 days). Raman spectroscopy and transmission electron microscopy were performed to confirm and evaluate the structure of the few-layer graphene nanosheets. GN-based membranes were prepared by vacuum filtration method using polyvinylidene difluoride supports. No swelling and pinholes were observed during ion the transport studies in water-based media.

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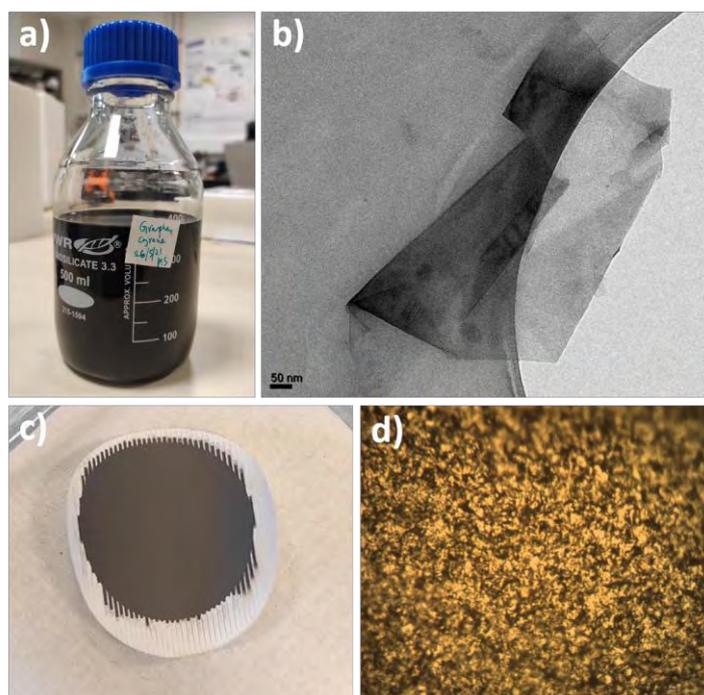


Figure 1: a) Photographic image of the as-prepared graphene dispersion in cyrene solvent. b) TEM image of graphene nanosheets. c) As-fabricated graphene-based membrane. d) Optical microscopy image of the graphene laminates.

A Single Particle LSPR Biosensor for Thrombin Activity Determination in Real-time

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Belonging to the Protease's family, a key example and probably the most clinically relevant nowadays is Thrombin that despite being involved in other cellular processes, as angiogenesis and inflammation, it is mostly known for its pivotal role in the coagulation of blood. Known by being involved in several diseases such as cancer, chronic inflammatory diseases, atherosclerosis and others,^[1] its activity is strictly regulated by a cascade mechanism involving activators and inhibitors in a feedback loop. Unfortunately, this implies that the correlation between the quantity/concentration of Thrombin present within a sample and its activity – which detrimental to understand the condition and often even its extent - is unreliable, mitigating its potential as biomarker. Additionally, and besides diagnosis and prognosis purposes a reliable proteolytic activity sensor can be crucial in developing protease-targeted therapies, or even in biochemical studies to understand the role of such enzymes.^[2]

Acknowledging this, and based on previous work,^[3] we resort to a dark-field microscopy setup with the ability to map single particle gold nanorods with nearly background free resolution to determine thrombinolytic activity in real-time. Using this construction, concentrations ranging from 1 – 300nM of active thrombin were detected in real-time. Besides the advantages aforementioned, this system has the potential for multiplexing while enabling monitoring proteolytic processes for long periods of time with sub-second resolution, since spurious effects such as photobleaching and photoblinking that are common in optical biosensors do not occur.

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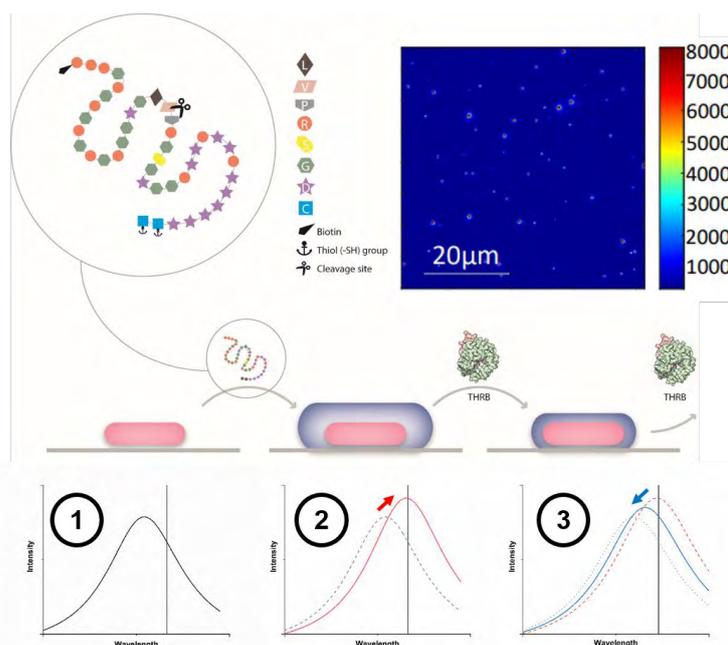


Figure 1: Schematics of the experimental design and principle.

Mini sensor based on graphene transistor for wine authenticity tracing by DNA detection

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Wine is one of the world's premium products susceptible to fraudulency. An analytical sensing method to detect adulteration and mislabelling for wines made of highly valued grape varieties is urgently required to protect the entire sectors in wine industry and viticulture business. Authenticity detection based on DNA analysis is a versatile technique because of the high specificity, molecular stability, and sensitivity of polymerase chain reaction (PCR) due to its amplification power [1]. This study presents a mini DNA sensor integrating graphene field-effect transistors (GFET). Monolayer graphene as the sensing membrane is modified with a pyrene-based linker through the π - π interaction to capture the amine-tagged DNA probe exposed to samples containing the complementary strands [2]. The portable system enables a rapid and straightforward screening of biochemical interactions onto the graphene chip through the Dirac voltage shift measurement. We specifically designed the probe DNA from the F3H gene of the *V. vinifera* (grapevine) to identify grape varieties from Douro (Portugal) Protected Designation of Origin (PDO). The integrated system shows a distinguished sensitivities for the detection of DNA hybridization in the PCR-amplified DNA samples from several grape varieties with different degree of mismatches, including Tinta Barocca and Tinta Francisca. The findings essentially denote the potentials of this miniaturized DNA sensor for the escalated level of detection in a complex sample matrix and the application for on-site detection.

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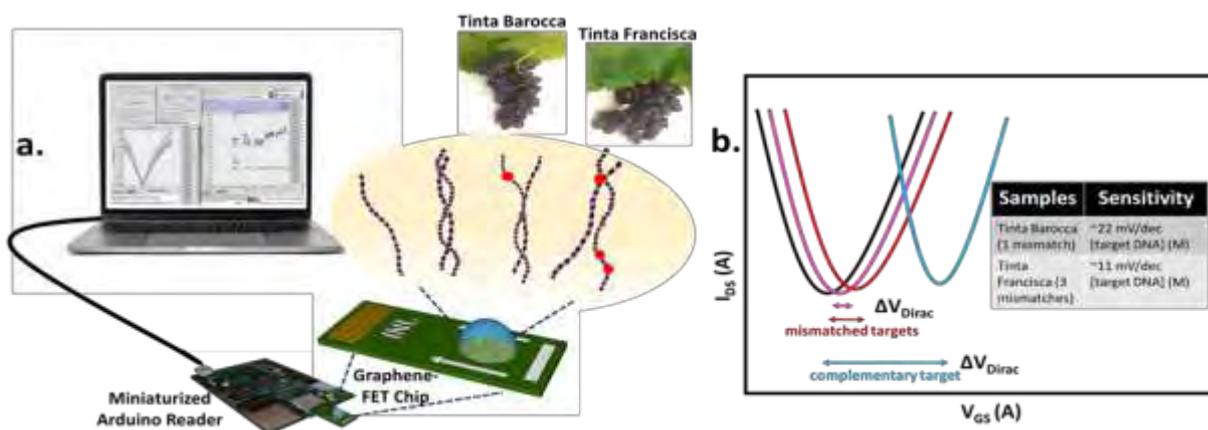


Figure 1: a. The mini sensor based on graphene-FET and b. the characteristics of transfer curves and sensitivity in DNA-based grapevine variety identification.

(Para)magnetic Hybrid Nanocomposites for Dual MRI Detection and Treatment of Solid Tumours

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Abstract

Cancer is the second leading cause of death worldwide, with approximately 18.1 million new cases and 9.6 million deaths in 2018.[1] Current treatment protocols (surgery, chemo-, radio- and immuno-therapy) have proved their utility in the clinic; nevertheless, they are unspecific resulting in low efficiency and severe side effects. Therefore, we have developed an innovative tool against solid tumors through a combination of early diagnosis and treatment (theranosis), that aims to reduce systemic toxicity. We have synthesized a hybrid nanocomposite including iron oxide (Fe_3O_4) and manganese oxide (MnO) magnetic nanoparticles (NPs) dispersed in a lipid matrix [2]. The chemotherapeutic drug, Doxorubicin was encapsulated in the lipid matrix (Fig.1). The lipid matrix allows the direct delivery of the drug to cells while the magnetic core allows the generation of heat under an alternating magnetic field (magnetic hyperthermia, MH), which enhances drug release from the nanocomposite. Furthermore, magnetic nanoparticles are ideal contrast agents (CAs) for MRI, allowing the early and non-invasive imaging of tumors [3]. The nanocomposite was characterized in terms of physico-chemical and functional properties, with a focus in its performance as an MRI contrast enhancer, MH effector and controlled drug delivery system. *In vitro* experiments to validate this (para)magnetic nanocomposite in Hs578T cell were also performed [2]. The resulting hybrid nanocomposite present a size of ~ 170 nm with a zeta potential of 29 mV. The particles exhibited great magnetic properties, which translated into a good dual T_1 - T_2 behavior in MRI. The r_1 and r_2 relaxivity values were 13 and $318 \text{ mM}^{-1} \text{ s}^{-1}$, respectively, which is higher than commercially available CA formulations. *In vitro* studies showed that cells presented a reduced viability when Doxorubicin was encapsulated, which indicates that encapsulation potentiates its effect. We also observed a reduced cell viability when cells were treated with the nanocomposite combined with MH induction, indicating a higher drug release.

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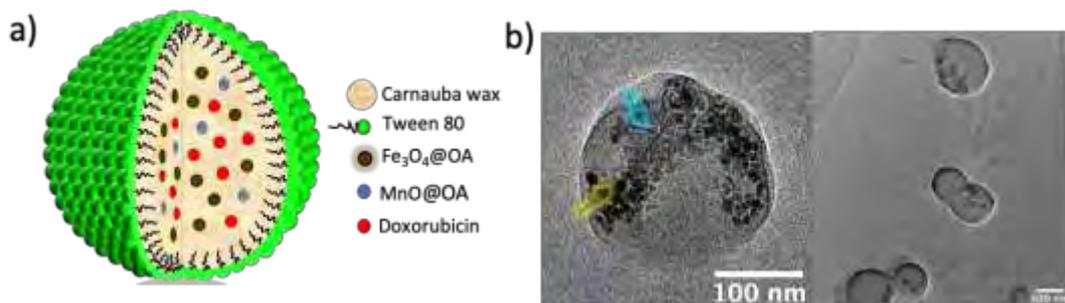


Figure 1: (a) Schematic representation of the hybrid nanocomposite and (b) respective TEM images (blue arrows highlight MnO NPs, yellow arrows highlight Fe_3O_4 NPs).

Bioactive coating via local surface functionalization of poly(L-lactic) acid for efficient tissue regeneration

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This work demonstrates an approach for functionalizing medical stainless steel 316L (SS316L) surface towards enhanced bioactive properties, providing the precise control of adhesion behavior for target proteins and cells. The approach is based on SS316L surface coating by poly (L-lactic acid) (PLLA) polymer thin film synthesized in α form and ordered gt conformer possessing a high degree of crystallinity at 48.8 %. PLLA is a biocompatible and biodegradable semicrystalline synthetic polymer that has considerable potential as a scaffold for tissue engineering, especially related to bone regeneration, mainly due to its polar properties [1]. The link of tissue regeneration with polar (piezo- and ferroelectrics) properties of materials was established by Fukada in 1991 [2], and still, this task has been keeping not sufficiently explored.

The functionalization approach was made via the application of patterned dc bias voltage. The local piezoelectric measurement demonstrates correlated out-of-plane and in-plane piezoresponses and robust polarisation switching reflecting the ferroelectric nature of PLLA at micrometer scale levels. The surface potential distribution measured after functionalization demonstrates distinct differences in work functions with respect to the sign of applied dc BV polarity, thus indicating the possibility to manipulate the electronic state of the PLLA surface to adapt the adhesion of target proteins and cells to promote its growth and proliferation.

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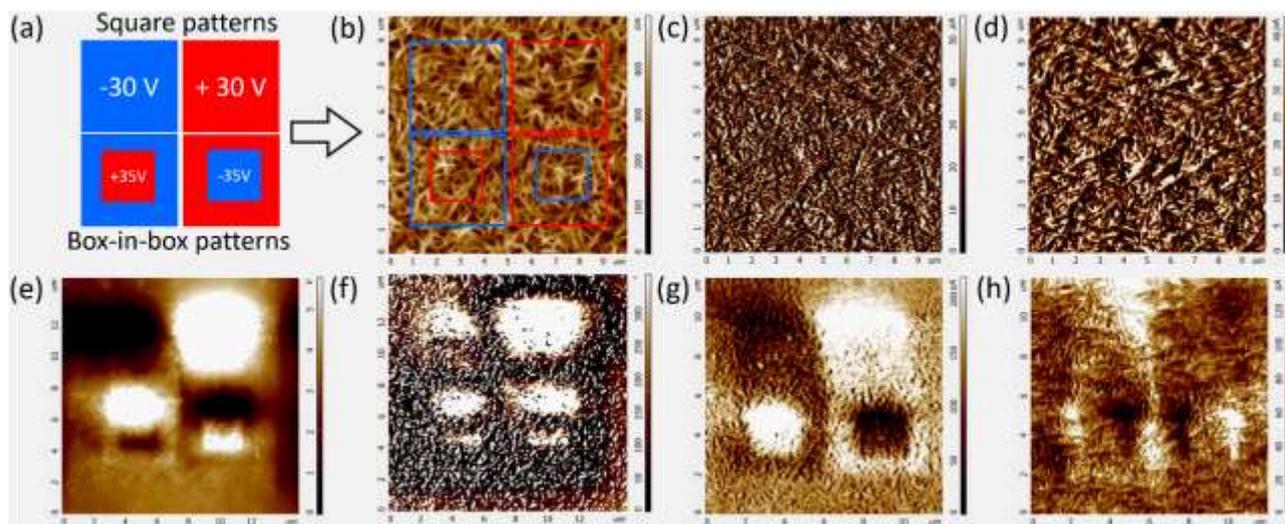


Figure 1: (a) A sketch of pattern schemes to apply the dc bias voltage to the surface of α form PLLA coating. (b) Topography and the corresponding pristine (c) OOP and (d) IP PFM responses before dc BV poling. (e) KPFM, (f) EFM, (g) OOP and (h) IP PFM scan images obtained after the application of patterned dc BV.

Application of nano-TiO₂ and micro-PTFE on Recycled Asphalt Mixtures for Superhydrophobic Functionalization

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The main objective of this research is to improve the efficiency and durability of the superhydrophobic capability on asphalt mixtures. In general, the benefits of this capability on materials are several, for example, water-resistance, anti-icing, antibacterial, contaminant-free, self-cleaning, anticorrosive, among others [1]. Through this type of functionalization, road engineering researchers seek to improve water repelling and resistance, and prevent ice formation on pavements [2–4]. Additionally, it generates the self-cleaning ability, relevant to remove dust from the surface. All these aspects are mostly related to the mitigation of friction decrease caused by water, ice, or even dust over the surface of the pavements. The superhydrophobic capability is achieved when the Water Contact Angle (WCA) between a water droplet and the material surface is higher than 150° [1]. In this research, three asphalt mixtures, type AC 10, were functionalized: R (reference), without any recycled material; F, with 30% reclaimed asphalt pavement (RAP); and A, with 30% steel slags (SS). The functionalization process consisted of two successive spraying coatings: i) spraying of a diluted resin epoxy and ii) spraying of a solution composed of nano-TiO₂ and micro-PTFE (under ethyl alcohol medium with a concentration of 4 g/L of each solute). The epoxy resin was diluted using butyl acetate with a proportion of 1:1 in mass. The cut asphalt mixture samples (25 x 25 x 15 mm³) were sprayed with 0.25, 0.50, 1, and 2 g of the diluted resin, resulting in a covering ratio of 0.1, 0.2, 0.4, and 0.8 mg/cm², and with 8 mL/cm² of the particles' solution both at room temperature. The wettability of the mixtures without any treatment, with only resin spraying coating and with both spraying coatings (resin and particles) was assessed by the Water Contact Angle (WCA). The results showed that F and R present similar initial WCA, 108° and 115° respectively, while mixture A presented a much higher WCA (131°). The spraying of the resin decreases the WCA, the higher resin content lead to lower WCA. The superhydrophobic capability was achieved for R and F samples with 0.25 and 0.50 g of resin spraying with particles. The mixture A achieved the superhydrophobicity only with 0.25 g of resin spraying with particles.

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Development of microfluidic-based tools to mimic the human gastrointestinal tract

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Introduction: The tremendous growth of nanotechnology applications in the food and feed arena, requires suitable methodologies to ascertain their safety and efficiency. Digestion in the human gastrointestinal tract (GIT) poses a harsh environment to which orally-administrated bioactive compounds may not resist. Also, the intestinal epithelium constitutes an additional barrier, which needs to be overcome in order to achieve absorption to the systemic circulation¹. Microfluidics offers the capacity to study valuable compounds in minute concentrations and small volumes (e.g., nanomaterials), thus paving the way to the fabrication of new platforms that will allow assessing the bioaccessibility and intestinal absorption of emerging nanoformulations. Here, we developed a modular microfluidic platform to simulate digestion in the human GIT and cell-based intestinal epithelial absorption (gut-chip). **Materials&Methods:** Microfluidic devices were designed using 2D and 3D CAD software and fabricated from PDMS following standard UV photolithography, rapid prototyping, and soft lithography techniques (Fig.1 A-B). On-chip digestion was quantified using a fluorescently-labelled casein derivative and compared to a standardised static digestion protocol². Cell-based gut-chips were fabricated by bonding two parallel channels separated by a semi-permeable PDMS membrane fabricated in-house. The membrane was pre-treated, coated with a mixture of extracellular matrix (ECM) proteins (collagen/matrigel), and seeded with the human intestinal epithelial cell line, Caco-2, at 1×10^5 cells/cm². Cell morphology and proliferation were assessed by immunocytochemistry of the tight junction protein occludin, with actin and nuclei counterstained using phalloidin and DAPI respectively. **Results&Discussion:** Fig. 2A shows that on-chip digestion was successfully achieved following a time-resolved kinetics profile in both gastric and intestinal phases. While the end-point fluorescence (Fig. 2B, green) was lower when compared to the current gold standard protocol, the results were consistent and reproducible, highlighting the potential of this miniaturised device to be used for *in vitro* studies of new nanomaterials. Gut-chips showed that Caco-2 cells were able to adhere and proliferate on the ECM-coated PDMS membranes (Fig. 1D). **Conclusion:** The present work contributed to the establishment of robust *in vitro* tools based on microfluidics to study the digestion and intestinal absorption of functional compounds designed for oral administration. Future work will focus on the introduction of biosensors to monitor relevant indicators (pH, temperature, transepithelial resistance) and on the development of a fully interfaced platform.

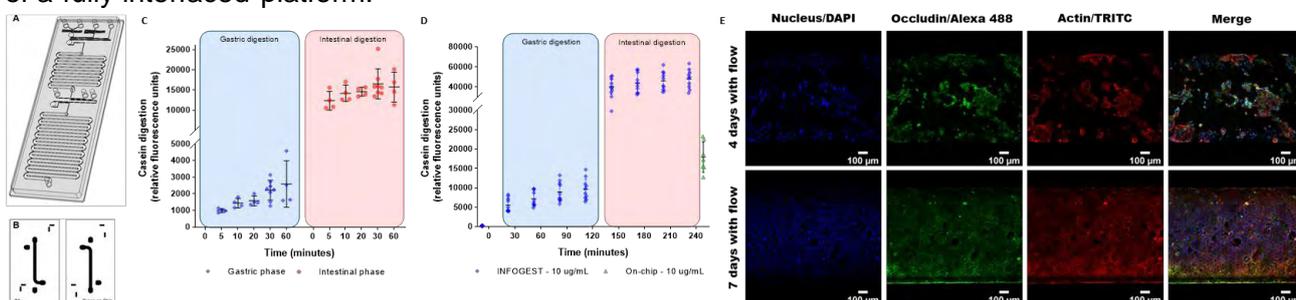


Figure 1: A-B. Representation of the digestion-chip design and gut-chip design (top and bottom slab), respectively; C. On-chip digestion of a casein reporter molecule ($10 \mu\text{g}\cdot\text{mL}^{-1}$). Digestion on-chip profile kinetics obtained by varying the flow rates ($12\text{--}1152 \mu\text{L}\cdot\text{h}^{-1}$) of the sample and simulated digestion fluids; D. Digestion following the static INFOGEST method of casein at $10 \mu\text{g}\cdot\text{mL}^{-1}$ (blue) and its comparison with the end-point of on-chip digestions (green); E. Confocal microscopy images of Caco-2 cells cultured on top of ECM-coated PDMS membranes following 4 and 7 days of culture under continuous flow ($30 \mu\text{L}\cdot\text{h}^{-1}$).

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Refractometric sensitivity comparison between different nanoparticle structures towards optical fiber sensors

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Plasmonic nanoparticles (NPs) are known to show localized surface plasmon resonances (LSPR), whose optical properties depend on NPs size, geometry, material and inter-particle coupling [1], [2]. Their refractometric properties also depend on the light coupling conditions, being the prism-based configurations the most used [3]. Recently, LSPR excitation with optical fibers have shown interesting results, with reports of both low and high refractive index (RI) sensitivity (RIS) [4], [5].

Herein, a comparison between such reports is made for a common optrode configuration based on a decladded section of a multimode fiber (MMF) coated with gold NPs. Some reports analyze their RI response only in terms of amplitude, showing wavelength insensitive RI response, as reported in [6], or works that show unusually high wavelength shifts. Such example is shown by Jia et al., [7], reporting a RIS of 2016 nm/RIU, with gold nanospheres (NS) of 80 nm. This shows great diversity when compared to gold NS on planar substrates, where typical RIS range from 50 to 100 nm/RIU [3]. To date, the mechanisms behind this RIS variability are not well understood, with erroneous attributions to hot-spots or interparticle coupling [7]. On the other hand, Otte et al. [8] proposed that by treating the NP region as a uniform region, resulted in modified dispersion curves, leading to great effective RI, thus changing greatly the sensor RIS properties.

In this work we will compare gold and silver NSs and analyze their RIS properties for the same optrode configuration, as the works here cited. The NPs synthesized procedure will be discussed and compared by their material properties. Preliminary results presented an overall high RIS for all the gold nanospheres, reaching a maximum of 4186 nm/RIU for the 35 nm gold NSs. The highest RIS reported on such NP geometry. Moreover, a nonlinear RIS increase was also observed. These results presented a great RIS increase when compared to the obtained 82 nm/RIU for the same gold NS deposited on a glass slide.

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Quantitative colocalization between cationic liposomes and DNA revealed by Fluorescence Cross-Correlation Spectroscopy

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COVID-19 mRNA-based vaccines have exhibited the importance of lipid-nucleic acid nanoparticles. One critical aspect in the development of such formulations is quantifying the extent of association (i.e. co-localization) between lipids and DNA, which thus far has been difficult to obtain quantitatively. Here we propose an approach based on fluorescence cross-correlation spectroscopy (FCCS) [1] to overcome this limitation [2]. The method consists of following the dynamics of lipids and DNA fluorescently labeled with two distinct dyes (red and green, respectively). By following the correlations between the motions of lipids and DNA the method is able to distinguish the cases where the lipid and DNA move together in the same particles, from those where non-complexed lipid and DNA move freely and independently (Figure 1). Hence, the co-localization between lipids and DNA can be determined. Importantly, the number of DNA molecules per lipid nanoparticle, which is an important parameter difficult to determine experimentally, can also be extracted.

FCCS therefore becomes a powerful methodology to understand the interactions between lipids and DNA/mRNA; understand their phase behavior and formulations; and to accelerate mRNA vaccine development. The methodology can also be extended to other colloidal systems involving association/dissociation between two nanosized species as long as they can be fluorescently labelled.

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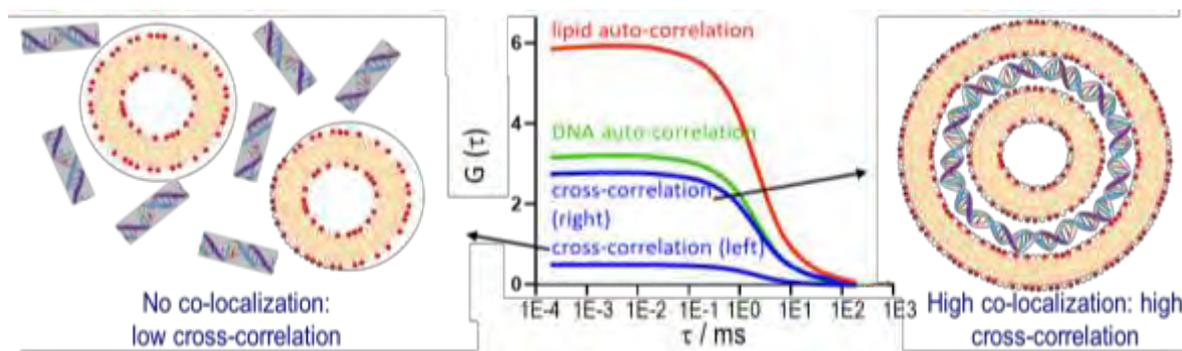


Figure 1: Illustration of the use of FCCS to monitor the formation of cationic liposome – DNA complexes. Liposomes and DNA are labelled with two spectrally-resolved dyes and their motions are analyzed simultaneously, which allows determining the individual auto- and cross-correlation functions. From the amplitude of the cross-correlation a quantitative measure of the co-localization between liposomes and DNA can be obtained. Non-bound liposomes and DNA have very low cross-correlation (left). Lipid-DNA complexes show high cross-correlation amplitudes (right)

Development of a new magnetically responsive device for localized cancer theranostics

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Cancer is one of the main causes of death worldwide and its occurrence has been increasing over the years. Due to the therapeutic inefficiency and severe side effects of conventional cancer treatments, the development of new cancer treatment options has been one of the most studied research areas. The development of new multifunctional systems that deliver therapeutic agents locally to the tumor site allows a more personalized and effective treatment. The present work focuses on the development a dual-stimuli responsive device composed of Fe_3O_4 magnetic nanoparticles (mNPs) and poly(N-isopropyl acrylamide) (PNIPAAm) microgels (MG) embedded in electrospun polymeric fibers capable of providing a simultaneous and local combinatory cancer treatment: chemotherapy and magnetic hyperthermia. mNPs with an average diameter of 8 nm were synthesized by chemical co-precipitation technique and stabilized with dimercaptosuccinic acid (DMSA) and oleic acid (OA) [1]. Thermoresponsive PNIPAAm MG were obtained by surfactant-free emulsion polymerization [2]. At room temperature, MGs are in a swollen state with a hydrodynamic diameter of around 1 μm . Above 32 $^\circ\text{C}$, their hydrodynamic diameter decreases, confirming their negative temperature response and Lower Critical Solution Temperature [3,4]. Poly(vinyl alcohol) (PVA) was used as fiber template and 10 wt.% of PNIPAAm MG and 10 wt.% of mNPs were incorporated in the fibers through colloidal electrospinning technique to produce dual-stimuli nanofibrous membranes with a bead-on-a-string morphology. The presence of MG and mNPs in the electrospun fibers decreases the membrane swelling ratio and increases its stiffness, raising its Young's modulus when compared to the plain PVA membrane. DMSA-mNPs appear to have a slight impact in the rise of rigidity of the membrane when compared to the OA-mNPs. Magnetic hyperthermia assays show that a higher concentration of mNPs leads to a higher heating ability, as expected. The composite membrane with 10 wt.% DMSA-mNPs shows the highest temperature variation, 5.1 $^\circ\text{C}$. Cytotoxicity assays were performed demonstrating that PVA membranes incorporated with PNIPAAm microgels and mNPs do not present any type of cytotoxicity and therefore could be used in biomedical applications. To assess adhesion, immunostaining analysis of focal adhesion (FA) protein vinculin and filamentous actin in different tumor cells lines (melanoma cells, WM983b, osteosarcoma, SaOs) was performed and compared with non-malignant cells (adult dermal fibroblasts). To assess proliferation, resazurin and 3D laser scanning confocal microscopy was used. Cell death was quantified by combining resazurin measurements and imaging of fluorescently probes, namely live/dead dyes (calcein-AM and Ethidium homodimer-1) and immunostaining with apoptosis markers (cleaved caspase-3). PVA/MG/NP displayed similar rate of cellular adhesion and the FA staining did not change. FA were more elongated in cell seeded onto PVA fibers when compared to collagen type I coated glass. These demonstrates that neither NP nor MG altered the affinity of cells to the PVA fibers. Proliferation was analysed within a period of 14 days, being the most dramatic changes observed amongst controls. This data suggests that the incorporation of MG and/or NP do not alter cellular responses in comparison with PVA alone. Currently, we are investigating the full potential of PVA/MG/NP to deliver chemotherapeutic agents in 3D cultures of tumor cells. Preliminary data shows that doxorubicin loaded NP/MG promote cell death. In the early future, we will incorporate doxorubicin loaded NP/MG into PVA fibers and analyse their ability to promote cell death in response to HFAFM.

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Gold nanorods as radiosensitizer agents on PC3 cells

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Abstract

Different structures of gold nanoparticles (AuNPs) are being extensively used in Radiotherapy (RT) because gold increased the sensitivity to radiation due to its high atomic number that can absorb high-energy gamma rays or X-rays and emit photoelectrons, Auger electrons, Compton electrons, and fluorescence photons.¹ Gold nanorods (AuNP_r) are gold nanoparticles with a rod shape, used to enhance the effect of ionizing radiation.²

After synthesized, the effect of the AuNP_r on radiosensitization using megavoltage energies RT was evaluated for in PC3 prostate cancer cell line (PCa). Cells were incubated with different concentrations of AuNP_r (0-1.0 mM) during 24h, then subjected to irradiation of 2,5 Gy per fraction, for 3 days, using a PRIMUS linear accelerator with 6 MV photon beam. After RT treatments, cell viability was analysed using PrestoBlue assay (*Invitrogen*TM), cell migration was explored doing the *in vitro* wound healing assay, and colonies assay was evaluated by microscopy.

In this work, we found that the AuNP_r displays a radiosensitization effect and it is dose dependent in PC3 cell line. These results are supported by decrease of viability and number of colonies produced.

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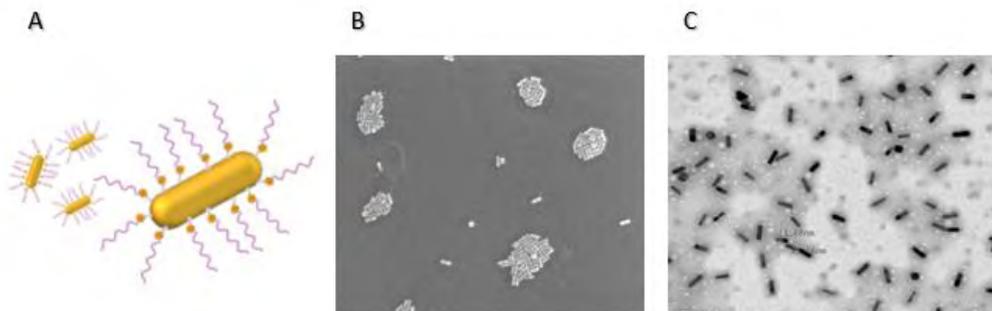


Figure 1: Scheme of AuNP_r with PEG, Scanning electron microscope (SEM, 200000x) and Transmission electron microscopy (TEM, 150000x) images.

Colloidal Synthesis of PbTe and SnSe for Thermoelectric Application

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The escalating demand for alternative clean energy sources requires the development of new and effective materials for energy recovery and conversion. Thermoelectrics (TEs) appear as a promising technology for global energy transition. When integrated into a real device, the best bulk TE materials have $zT \approx 1.2$, but an average $zT = 2-4$ is necessary for TE energy conversion. Fortunately, it has been shown that creating nanostructured composite devices in new geometries can increase TE efficiency. Also the preparation of TE materials through solution-based methods offers a promising path towards minimizing the TEs production cost. We investigated colloidal synthesis of the phase-pure PbTe and SnSe nanomaterials, since they are promising TE materials with $zT_{\max} > 2.4$. These particles were obtained by a large-scale synthesis similar as we previously reported [1]. The PbTe and SnSe materials were characterized by scanning electron microscopy (SEM) revealing an interesting shape and size of the resultant particles as observed on Figure 1. Further TE characteristics of spark-plasma-sintered PbTe and SnSe, namely, thermal conductivity, electrical resistivity, Seebeck coefficient and zT , have also been investigated and discussed.

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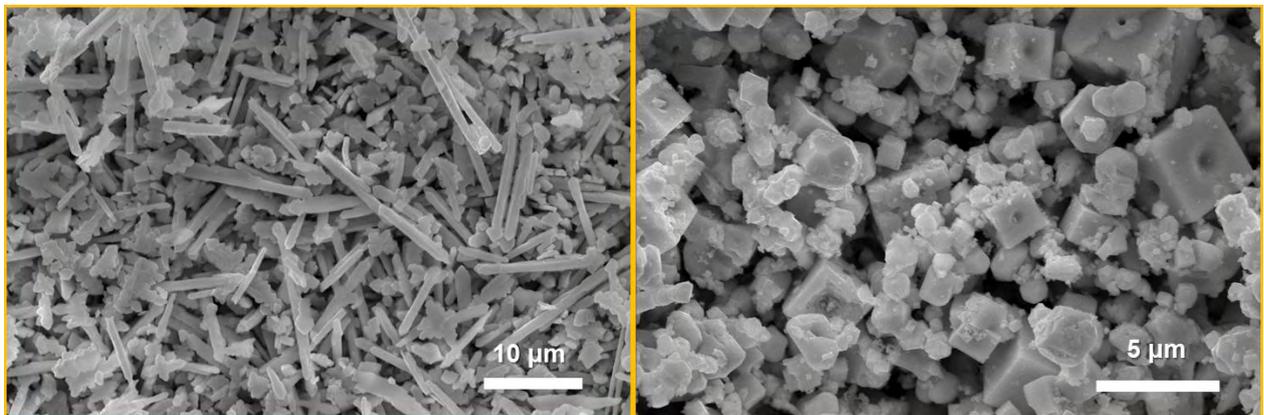


Figure 1: Scanning electron microscopy images of SnSe (on the left) and PbTe synthesized particles (on the right).

A carbon layer coated porous silicon anode with high capacity for high energy density lithium ion batteries

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Abstract

Lithium-ion batteries (LIBs) are currently one of major commercially available energy storage devices that are widely adopted in mobile phones, laptops and other consumer electronics. They also show substantial promise for the electrification of vehicles, contributing to zero-emission transportation. However, for electric vehicle (EV) applications the traditional graphite anode materials presently being used in commercial LIBs cannot satisfy the demand for high energy density, and thereby are difficult to offer a driving range comparable to the conventional internal combustion engine.[1-3] To improve the energy density of LIBs, silicon (Si) has been proposed to be a promising alternative to graphite because of its high theoretical specific capacity. The large volume change of Si during the Li insertion/extraction processes, however, would lead to severe pulverization of anode, poor electrical contact of active materials with the current collector, unstable solid–electrolyte interphase (SEI), and eventually to irreversible capacity fading.[4,5] Although significant progress has been made to address these issues through nano-silicon based materials design, there is still a pressing need for continuous improvement of Si anode's performance and further reduction of the costs, considering the market penetration. In this presentation, we will report our recent progress in developing a scalable, low-cost process for preparing nanoporous silicon-carbon composites, which is realized by wet chemical processing of ferrosilicon, followed by a carbon layer coating process. By optimizing the synthesis conditions, a yield of 87.5% is achieved for the nanoporous Si on gram-scale production in the lab. Because of the hierarchical micro-nano scale architecture, the nanoporous silicon anode delivers an initial reversible capacity as high as 2993 mAh/g and an initial Coulombic efficiency of 82 %, which are markedly higher compared to the commercial Si nanoparticles. The nanoporous silicon-carbon composite active materials hold great promising for use to improve the energy density of the next generation lithium-ion batteries.

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The interplay of nanocomposites co-assembly with peptide-based gels as a strategy towards on-demand drug release

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Self-assembled peptide-based hydrogels are highly advantageous as nanocarriers for antitumour drug delivery, owing to the low critical gelation concentration, easy tailoring of the mechanical properties, biocompatibility and similarity to the extracellular matrix [1]. The solvent pockets allow the encapsulation of composites, such as magnetic nanoparticles and liposomes. The combination of gels with magnetic nanoparticles towards magnetic gels provides a means for the real-time remote control of gels' properties. These properties can be further improved through the combination with liposomes as it enables the compartmentalization of drugs that can be released in a sequential and on-demand manner [2,3].

However, implementing a stimulus can become a cumbersome task. Often, it requires screening different structures to obtain gels with suitable properties, and drugs might not be well encapsulated and/or cause undesirable effects on the gel's properties. To overcome this challenge, a design strategy was developed that enabled the modulation of release of the chemotherapeutic drug doxorubicin through the interplay of (di)phenylalanine-coated magnetic nanoparticles, PEGylated liposomes and doxorubicin co-assembly in dehydropeptide-based gels. The co-assembly of the nanoparticles with the gel network is displayed in figure 1. The integration of liposomes as storage units enabled the tuneability of both passive and active doxorubicin release through a thermal and low-frequency alternating magnetic field trigger, which makes this design strategy promising for future developments on the control of drug release.

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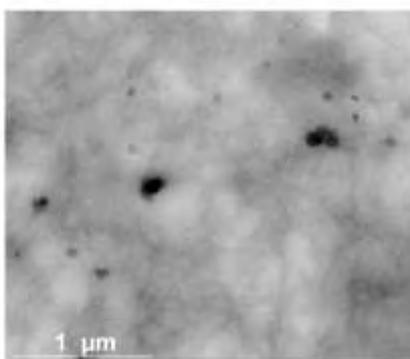


Figure 1: Transmission electron microscopy image of phenylalanine-coated nanoparticles co-assembled with the hydrogel network.

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Portable SERS-based detection system for ultra-detection of H₂S

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Hydrogen sulphide (H₂S), a product obtained by sulphate reducing bacteria, presents a high risk for aquaculture sector. This molecule with high toxicity, even at low concentrations, is responsible to increase the susceptibility of marine organisms to disease. To avoid this, different sensors, with the limit of detection in μM range, are used by the industry to detect this molecule. However, 1.6 μM is established as the highest concentration that should be detected in aquaculture systems. Thus, it is imperative the development of sensors to detect H₂S in water at lower concentration (nM range).

In this work, we are developing a portable surface-enhancement Raman scattering (SERS)-based sensor in order to decrease the limit of detection of H₂S. Over the last decades, anisotropic noble metal nanostructures are being exponentially used because offer large enhancement factors and good reproducibility, allowing single-molecule detection by SERS. Specially, gold nanostars (GNSs) that allow to reach an enhancement factor up to 10¹², by concentrating their electromagnetic field in the limit of their sharp branches using the core as an electron reservoir [1], [2]. Taking this advantages into consideration, we are immobilizing SERS substrate (GNSs) on poly (methyl methacrylate) (PMMA) (8 mm³) and post-functionalized it with a molecular probe that responds to the presence of H₂S, such is the case of 6-mercapto-striazolo(4,3-b)-s-tetrazine (MTT) [3] and 4-Mercaptobenzoic acid (4-MBA), by displacement of these molecular probes and consequent decrease in SERS signal. This cubes are then integrated into a microfluidic device (consisting in an inlet, a reservoir that acts as sensing area and an outlet) (figure 1) improving the sample delivery to the GNSs and reduction of the acquisition times for H₂S detection using a portable Raman. Through this portable sensor, we have been able to achieve a detection limit in the nM range for Na₂S-spiked water samples.

Acknowledgments. This research is funded by ERA-NET Blue Bio COFUND #81 project - DIGIRAS

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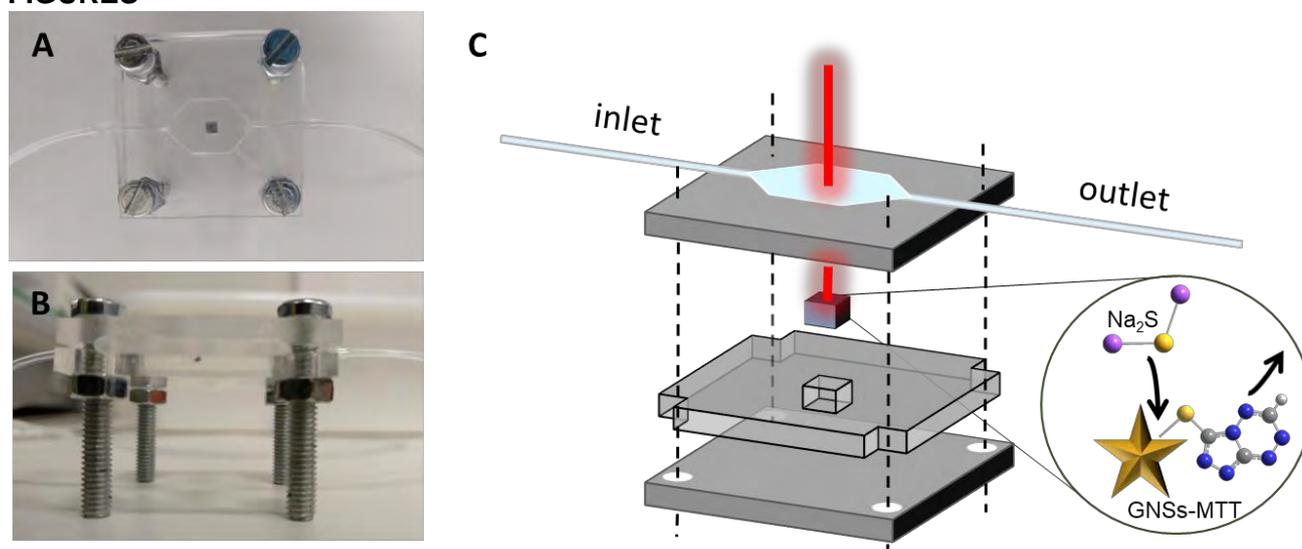


Figure 1: H₂S SERS-based sensor prototype. (A) from top (B) from side (C) schematic representation.

Highly Dispersed Noble Metal-Based Carbon Nitride as Efficient Electrocatalytic/Photocatalytic Hydrogen Evolution Reaction Catalysts

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Abstract

Hydrogen (H₂), with a high energy density and environmental friendliness, is considered one of the most promising clean energy carriers. Water splitting to generate H₂ by electrocatalytic/photocatalytic processes is a promising technology for renewable energy storage. However, the widespread deployment of water electrolyzers requires the development of efficient and stable catalysts containing minimal platinum group metals (PGMs) for the hydrogen evolution reaction (HER). Electrocatalytically active catalytic species can be used as co-catalysts in photocatalysis processes [1]. Hence, advanced catalysts combining high electrocatalytic performance with high photocatalytic performance are highly desired. Ruthenium and iridium (Ru, Ir)-based materials have drawn increasing attention for catalyzing the HER, which have been demonstrated both theoretically and experimentally to possess good HER performance [2,3]. Nevertheless, the utilization efficiency of noble metals seems still unsatisfactory, which is restricted by the relatively large particle size, wide size distribution, and high loading mass to achieve decent HER performance. Despite some recent progress in electrocatalytic HER using Ru and Ir-based catalyst, the use of Ru and Ir in visible-light-driven photocatalytic HER processes has been hindered by the inefficient transfer of electrons from the photosensitive material to the metal. Graphitic carbon nitride (gCN) has attracted increasing interest owing to its suitable bandgap (2.7 eV), excellent stability, and the abundance of free N-containing groups on its surface, which can anchor the metal species [4]. However, there are by far only a few reports on highly dispersed Ru and Ir stabilizing on the gCN support for photocatalytic HER. In this presentation, we will show our recent progress in making atomically dispersed Ru and Ir catalysts supported on gCN (Ir-gCN, Ru-gCN) by a simple and cost-effective hydrothermal approach. Thanks to the strong metal-support interaction (SMSI) between the noble metal and gCN, Ru and Ir are dispersed on gCN in the form of single-atoms and ultrafine sub-nanometric clusters. Impressively, the Ir-gCN and Ru-gCN catalysts with ultra-low metal loading exhibit superior catalytic activities for both electrocatalytic and photocatalytic HER, which can be attributed to the ultra-small catalyst size and high degree of dispersion of the active sites. Significantly, excellent durability has been also achieved benefiting from the SMSI. This study provides a potential strategy for developing high-efficiency, stable and multifunctional catalysts for electrochemical energy conversion.

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Versatile Micromotors for Photocatalytic Environmental Remediation

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Environmental degradation issue is a global concern. Great efforts have been made to develop efficient and green approaches for wastewater treatment. Self-propelled nano/microrobots are the forefront of nanotechnology, holding great promise for environmental remediation. Visible light driven semiconductor photocatalyst would be the great catalyst to power such micromachines for environmental remediation. BiVO_4 has attracted researchers' great interest. However, its drawbacks such as significant recombination of photogenerated electron-hole pairs, poor electrical conductivity and slow hole transfer kinetics limit its applications. To enhance the photocatalytic efficiency, we elaborately develops light-responsive tubular micromotors with smart material design strategy: BiVO_4 is robust visible light absorber; ZnO nanorod arrays act as electron transfer channel; reduced graphene oxide (rGO) films function as electron acceptor; and Co-Pi serves as hole acceptor and catalytic site. Herein, we established novel tubular Co-Pi/ BiVO_4 / ZnO /rGO micromotors, studied the comprehensive performance of micromotors in the polluted water with three types of contaminant models (i.e. dye, explosive and bacteria model); and integrated abundant micromotors in 3DP-motor and demonstrate the pilot-scale test in artificial $5 \times 5 \text{m}^2$ pool for environmental remediation, as illustrated in Figure 1. This work is sponsored by the Marie Skłodowska-Curie Actions (MSCA) Individual Fellowship.

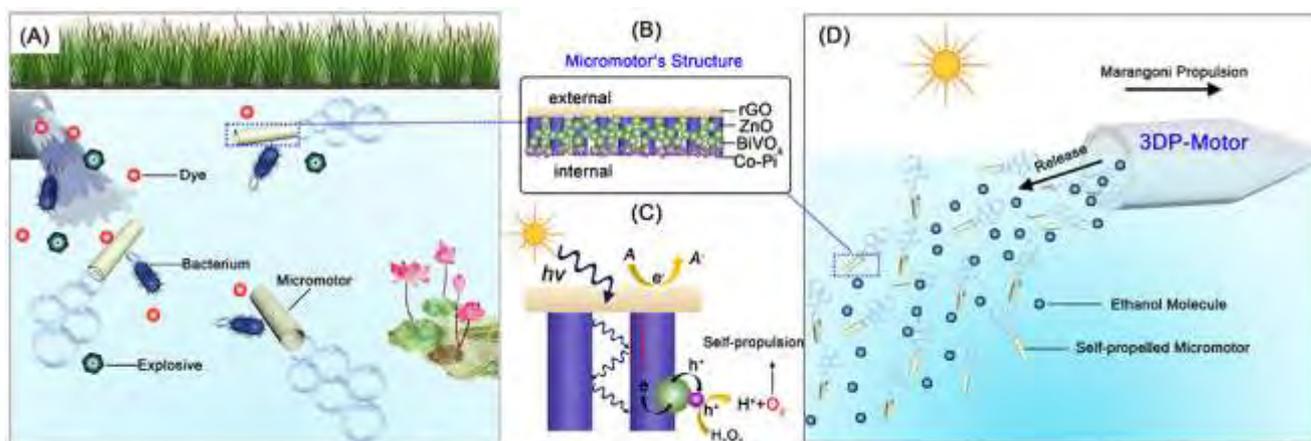


Figure 1: Schematic illustration of (A) versatile micromotors dynamically degrading dyes and explosives and killing bacteria in contaminated water, (B) structure of the designed micromotor, (C) design strategy of Co-Pi/ BiVO_4 / ZnO /rGO: (i) increased light absorption and charge generation in both BiVO_4 and ZnO through light trapping effect of the nanorods, (ii) electron injection into ZnO nanorods followed by prompt electron transport along ZnO nanorods, (iii) electron collection and storage in rGO for reduction reaction and (iv) hole transfer to Co-Pi for efficient water oxidation to generate oxygen bubbles for self-propulsion of micromotor, (D) 3D-printed millimeter-scale motor releasing micromotors and ethanol molecules.

Abstracts Flash Poster

Xanthan-Fe₃O₄ Nanoparticle Composite Hydrogels for Non-Invasive Magnetic Resonance Imaging and Magnetically-Assisted Drug Delivery

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A biocompatible xanthan gum (XG)-based drug-loaded magnetic nanocomposite hydrogel with optimized rheological properties was designed, synthesized and *in vitro* validated as a long-acting delivery system able to minimize off-target side effects and locally provide non-invasive magnetic resonance imaging. Both a hydrophilic antifungal drug and magnetic iron oxide nanoparticles were simultaneously encapsulated in a chemically-modified XG-polysaccharide matrix. In addition to an enhanced drug activity compared to the free drug, the magnetic component of the final hydrogel enabled an extra thermal-induced control over the drug delivery profile by magnetic hyperthermia, as well as a concentration-dependent shortening of the water protons' relaxation time at a clinical field of 3T, confirming its potential use as a T₂-MRI-based theranostic agent.

Altogether, these properties open a new dimension for the application of these versatile magnetohydrogels, from traditional topical uses to more internal surgery interventions in dentistry, oncology or wound healing of critical skin damages and infections.

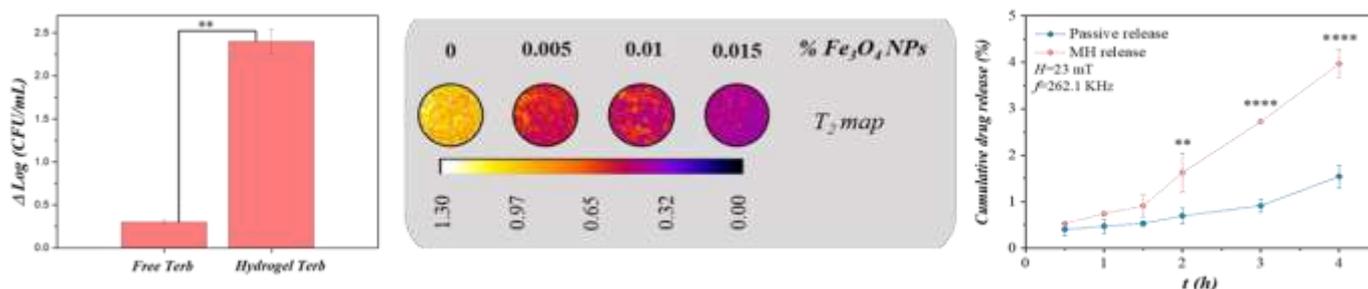


Figure 1: Left. Improvement of terbinafine antifungal activity (50 μg) incorporated into the hydrogel compared to free terbinafine. Center. T₂-weighted color map of hydrogels with different Fe₃O₄ MNPs loadings. Right. Cumulative passive release profile of terbinafine from the magnetic hydrogel XG/MXG2-10 with and without magnetic hyperthermia

Humidity and Temperature embedded textile sensor based on Graphene

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Textile electronics allows the integration of electronic devices in everyday life textile objects. However, sensing materials must be lightweight, imperceptible, low energy consumption and be flexible without compromising the textile characteristics. Therefore, it is required advances in materials and manufacturing processes combining flexibility, electrical properties of semiconductors and metals with solution and low temperature processing [1]. To achieve wearable electronics full potential, Graphene, a 2D material, with its flexibility, transparency, and high electrical conductivity [2], is suitable for textile electronics, as we recently demonstrated by developing a textile coated with graphene with sheet resistance lower than $1 \text{ k}\Omega \text{ sq}^{-1}$, while maintaining the textile mechanical properties [3, 4].

Wearable temperature and humidity sensors are versatile sensors as these can be used for body and environment monitoring to detect pathologies, or athlete's capabilities during their sport activity. Existing wearable systems lack flexibility, are uncomfortable, do not withstand washing and bending cycles.

Taking advantage of Few-Layer Graphene (FLG) properties and solution processability, we developed a humidity and temperature dual resistive sensor embedded in a textile capable of overcome bending and washing cycles, preserving their physical and mechanical properties. Our flexible sensor presents humidity sensitivity values of $-2.32 \cdot 10^2 \text{ \%}^{-1}$ and $-1.52 \cdot 10^{-1} \text{ }^\circ\text{C}^{-1}$ for temperature, 4 and 1 times higher than similar sensors (fig. 1) [5], demonstrating their potential for environmental and biological monitoring.

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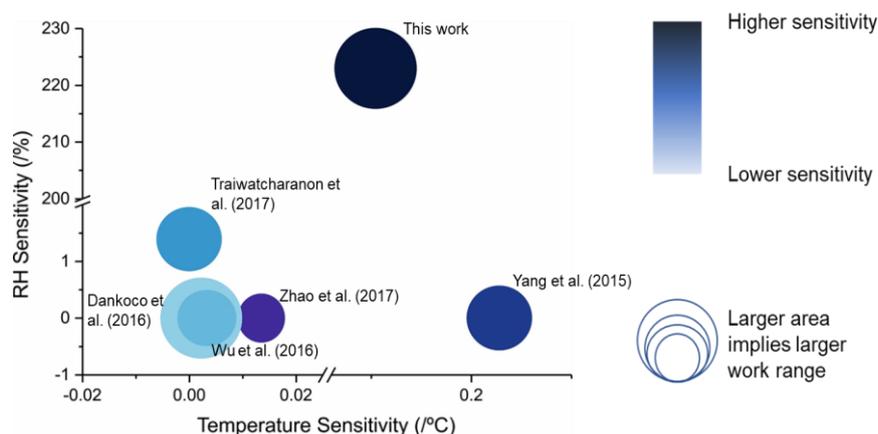


Figure 1: Comparison of our sensor with other similar flexible temperature and relative humidity sensors sensitivities.

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Abstracts ePoster

Atomic Layer Deposition of Al₂O₃/Ta₂O₅ Multilayer Gate Dielectrics for Low-Temperature IGZO TFTs

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The implementation of a multilayer stack as the gate dielectric in a thin-film transistor (TFT) enables the resulting material to display a combination of the benefits of both materials composing the stack. With the purpose of achieving a high- κ dielectric with low leakage current and a high breakdown field, thin films consisting of Ta₂O₅ and Al₂O₃ were grown at 225 °C and 200 °C, respectively, both as multilayers and single layers, by atomic layer deposition (ALD). The rationale was to use Ta₂O₅ for a high dielectric constant, with Al₂O₃ providing a large band offset to wide bandgap oxide semiconductors as indium-gallium-zinc oxide (IGZO). The precursors/reactive elements were tantalum ethoxide, Ta(OEt)₅, and water for Ta₂O₅, and trimethyl-aluminium (TMA) and water for Al₂O₃. Ta₂O₅ and Al₂O₃/Ta₂O₅/Al₂O₃ stacked thin films were deposited in metal-insulator-metal (MIM) structures and as gate dielectrics in sputtered IGZO bottom-gate TFTs, with thickness ranging between 50 nm (single layers) and 70 nm (multilayers). The insulating thin films were characterized by capacitance and current-voltage measurements, ellipsometry and Raman spectroscopy. The ALD processes were optimized to maximize the refractive index seen by ellipsometry (denser films) and to ensure that no Raman peaks associated with residual precursor or reactant were present. The Ta₂O₅ thin films showed a dielectric constant of 20, current density of 2.66×10^{-1} A.cm⁻² at 1 MV.cm⁻¹ and breakdown field of 1.36 MV.cm⁻¹, the Al₂O₃ thin films showed a dielectric constant of 8, current density of 2.61×10^{-8} A.cm⁻² at 1 MV.cm⁻¹ and breakdown field higher than 4 MV.cm⁻¹, while the multilayer thin films exhibited a dielectric constant of 11, current density of 2.06×10^{-5} A.cm⁻² at 1 MV.cm⁻¹ and breakdown field of 2.90 MV.cm⁻¹. Moving to IGZO TFTs, while the Ta₂O₅ gate dielectric resulted in the largest field-effect mobility (μ_{FE}) of 20.92 cm².V⁻¹.s⁻¹, the best balance among device characteristics was achieved with the multilayer gate dielectric, which presented μ_{FE} of 12.62 cm².V⁻¹.s⁻¹, turn-on voltage (V_{on}) of 20 mV, on/off ratio >10⁵, and subthreshold slope (S) of 90 mV.dec⁻¹. These performance metrics are similar to state-of-the-art IGZO TFTs reported worldwide, with the advantage of ultra-low operating voltage (transconductance saturation for $V_{GS} < 1.3$ V) owing to the 70 nm thick ALD multilayer gate insulators. Regarding positive gate bias stress measurements, a negative threshold voltage shift (Δ_{VT}) during stress was verified for Ta₂O₅, similarly to our previous findings for sputtered Ta₂O₅ [1], while a positive and larger magnitude Δ_{VT} was recorded for Al₂O₃, with a lower time constant (τ). The multilayer stack revealed an interesting route to minimize stress effects, showing the lowest Δ_{VT} after 3 h stress (0.55 V) among the three gate dielectric configurations. By further tuning of the stack composition, one can achieve a complete cancelation of the two competing degradation effects of Ta₂O₅ and Al₂O₃ and suppress Δ_{VT} [2].

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Optical Absorption Edge Shift in Rippled 2D InSe Flakes

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Abstract

Indium selenide (InSe) is a semiconductor that belongs to transition metal monochalcogenides (MX) 2D materials [1]. It is an interesting 2D material due to its optical, electronic, and technological applications e.g., solar energy conversion, laser, diodes, and infrared devices [1-2].

InSe is a direct-band-gap semiconductor in bulk (1.2 eV), but it turns into indirect band gap when its thickness is reduced to a few nanometers due to confinement effects [3]. Furthermore, the band gap of InSe flakes can be modulated by strain engineering technique.

In the present work, 2D InSe samples have been fabricated by mechanical exfoliation of bulk, and deposited on a flexible and transparent substrate, previously stressed by uniaxial force [1]. The optical absorption edge of rippled InSe flakes is measured by a scanning micro-transmittance technique. Results indicate an optical absorption band-edge shift up to ~0.3 eV between crest and valleys regions.

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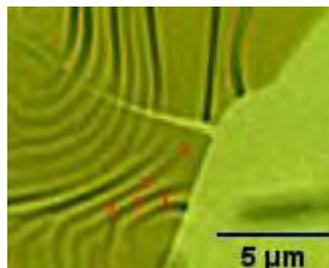


Figure 1: Transmission-mode optical microscope image of 7 layers of InSe wrinkled. The crosses indicate the region where spectra were registered.

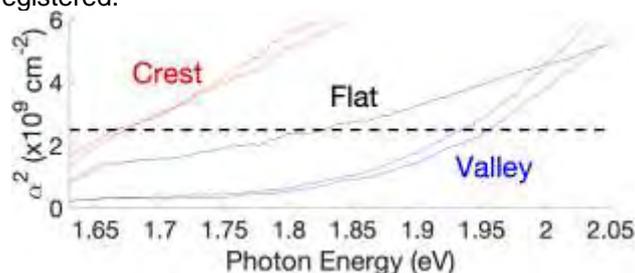


Figure 2: Optical absorption spectra at different crest (top), valley (bottom) and flat regions.

Manipulation of Majorana bound states in proximity to a quantum ring with Rashba coupling

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The quest for Majorana zero modes in the laboratory is an active field of research in condensed matter physics. In this regard, there have been many theoretical proposals. However, their experimental detection remains elusive. In this article, we present a realistic setting by considering a quantum ring with Rashba spin-orbit coupling and threaded by a magnetic flux, in contact with a topological superconducting nanowire. We focus on spin-polarized persistent currents to assess the existence of Majorana zero modes. We find that the Rashba spin-orbit coupling allows for tuning the position of the zero modes and has sizable effects on spin-polarized persistent currents. Our results pave the way towards probing the existence of Majorana zero modes.

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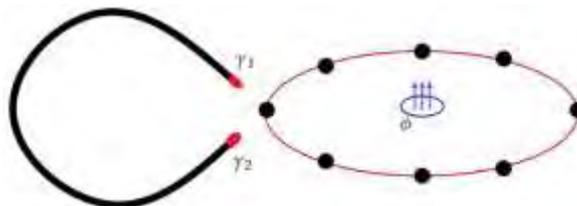


Figure 1: Sketch of a quantum ring threaded by a magnetic flux interacting with two Majorana bound states at the end of a p-wave superconducting wire.

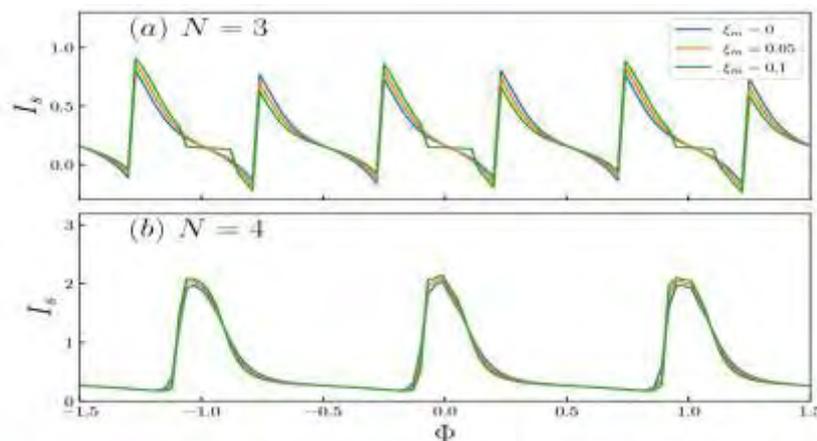


Figure 2: Spin persistent currents for (a) $N=3$ and (b) $N=4$ site ring with Rashba spin-orbit interaction, interacting with two Majorana bound states. Colours are used to indicate the interaction between the two Majorana bound states.

Impedimetric biosensor of heavy metals based on self-assembled HRP/gold nanoparticles/ ferrocenylurea DAB dendrimer monolayers

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Heavy metal ions have entered into the environmental life cycle through the pollution of soil and water as a consequence of industrial development [1], been lead and copper related causes of many heavy metal-related diseases [2]. Lead can cause gastrointestinal, neuromuscular and neuropathological symptoms [3]. Concurrently, copper has been connected with neurodegenerative disorders such as Parkinson's, Alzheimer's, and Prion disease [4]. The biosensor is based on the direct electrochemistry of horseradish peroxidase (HRP) immobilized on the self-assembled monolayers (SAMs) of gold nanoparticles, a DAB dendrimer of first generation functionalized with thiolated and ferrocenylurea groups, and colloidal gold nanoparticles of 5 nm. This modified electrode was very effective to the direct electrochemistry of HRP and showed high sensibility and operational range in the hydrogen peroxide determination. These properties make possible the development of a biosensor based on the selective inhibition of the immobilized enzyme caused by the metal ions, which results in a decrease in the response to hydrogen peroxide proportional to the quantity of ion present in the test solution [5] and an increase in the resistance of electrode surface. Usually, most of the inhibition-based biosensors are amperometric, although some, based on electrochemical impedance spectroscopy (EIS), have been developed [6, 7]. In this work, a new inhibition-based biosensor for the indirect determination of toxic lead and copper ions is reported. EIS has been successfully used as a detection signal for the determination of Pb^{2+} and Cu^{2+} ions. Complemented by amperometric analysis, a linear response between 0.05 and 1.5 $mg L^{-1}$ was obtained for both ions, with detection limits of 0.27 $\mu g L^{-1}$ and 0.77 $\mu g L^{-1}$ for Pb^{2+} and Cu^{2+} .

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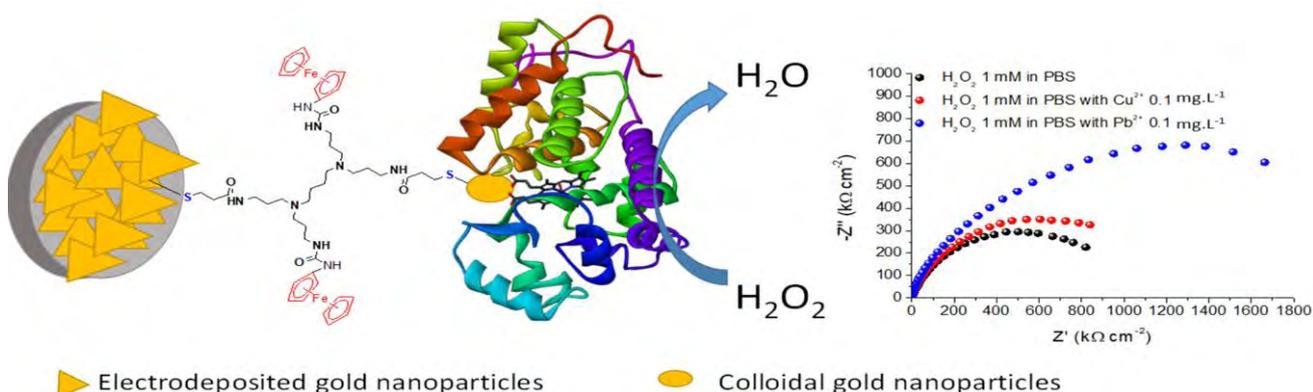


Figure 1: Scheme of the biosensor operation and its impedance response in the absence and presence of Cu^{2+} and Pb^{2+} .

Isolation and concentration of acute myeloid leukemia blasts in minimal residual disease using a microfluidic system

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Acute myeloid leukemia (AML) is characterised by the accumulation of immature myeloid progenitors in the bone marrow, interfering with the normal production of blood cells. This type of leukemia is the most common in adults and is frequently associated with poor outcomes and response to conventional therapies, particularly in older individuals^[1,2]. Unfortunately, the majority of the patients that can achieve clinical complete remission after the conventional treatment ultimately relapse due to the persistence of some residual cells that remains undetectable, condition called minimal residual disease (MRD)^[3]. Thus, an earlier and accurate diagnosis of MRD would allow for a better prognosis and also better follow up of the patients. Over the last years, microfluidics has demonstrated to be one of the technologies with potential to overpass the limitations of the conventional technologies. This technology is a powerful tool for the isolation and concentrations of rare cells from biological fluids towards earlier cancer diagnosis^[4,5]. Thus, this work aims to develop a microfluidic system for the isolation of leukemic blasts based on positive selection. First, in order to maximise cell-to-surface interaction and consequent attachment, distinct microfluidic devices composed by micropillars with different geometries and also a herringbone were designed and fabricated. Then, for the optimisation of the microfluidic devices, some parameters were tested, including different functionalisation strategies for the immobilisation of the antibody in the surface and flow rates. AML cell lines with known concentrations were spiked peripheral blood mononuclear cells obtained from healthy donors and run through the devices. Once the optimal conditions are found and the best isolation efficiency obtained, we expect to perform a validation of this microfluidic system in a cohort of AML patients at different stages of the disease.

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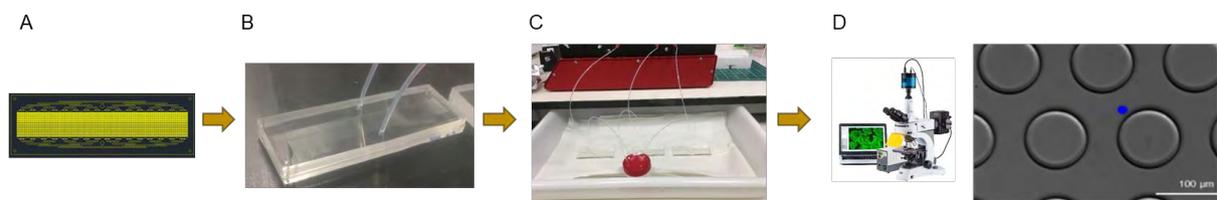


Figure 1 Overview of all process from the design to the analysis of the microfluidic devices. Design of the devices composed by pillars in the AutoCAD (A); Fabrication of the devices using a polymer (PDMS) (B); setup of the experiment during the running of the samples (cells+PBMCs) in the devices and analysis in the fluorescence microscope (D).

Characterization of an oxygen biosensor based on bilirubin oxidase enzyme efficiently tethered to a nanostructured carbon paper transducer

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Oxygen bioelectrocatalysis has potential relevancy for different fields namely industry, clinical and energy field, specifically through the development of efficient biosensors or biofuel cells capable to produce energy for low-power electronic devices. In an energy-demanding world, the design of self-powered biosensors is a very interesting possibility to be applied in the aforementioned fields. The recurrence to enzymes for catalytic processes enables high specificity to the substrate / target analyte at mild conditions. More concretely, the enzyme bilirubin oxidase (BOx) is a multicopper oxidase that performs the catalysis of oxygen naturally (acting as a co-substrate) and very efficiently. In electrochemistry, a direct electron transfer feature is easily attained with this enzyme even when immobilized simply by adsorption to a transducer. However the employment of certain tethering agents in immobilization can orientate the enzyme and lead to improved stability of the system [1]. Another important part in the bioelectrocatalytic system is the electrode nature itself. One relevant example is carbon fibre paper (CP) which is commonly used in both fuel and biofuel cells due to its high porosity and surface area, excellent mechanical and electronic properties [2]. In this sense, the objective of this work was the development of a simple but highly efficient oxygen biosensor that consisted in the immobilization of BOx to a multi-walled carbon nanotube (MWCNT) modified CP through pyrene-based bifunctional crosslinker. The electrode nanostructuring with MWCNT not only enables a higher electron transfer capacity but also allows anchoring of the enzyme. Cyclic voltammetry was used to assess enzyme immobilization, with the bioelectrode achieving a current density of $-114 \mu\text{A cm}^{-2}$ at 0 V in the presence of O_2 (air-saturated) compared with only $-31 \mu\text{A cm}^{-2}$ in the absence of O_2 . The sensitivity was determined by amperometry with the biosensor achieving a value of $580 \mu\text{A cm}^{-2} \text{mM}^{-1}$ and the limit of detection corresponded to about $1 \mu\text{M}$. To note also the great stability of the biosensor which practically maintained the sensitivity value after 5 days in storage at 4°C (106% compared to day 0).

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