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Index

Foreword

On behalf of the Scientific and Technical Committees we take great pleasure in welcoming you for the first edition of the nanoPT International Online Conference (NPTO2020).

The two-days NPTO2020 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) and considering that all major scientific and technological conferences are being cancelled or postponed worldwide until the end of 2020.

NPTO2020 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.

20 high profile talks from 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 nanoPT.

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Speakers/Orals/FlashPosters/Posters list: Alphabetical order

Authors	Session	Page
Isaac Alcon (Freie Universität Berlin, Germany) Quantum Interference Engineering of Nanoporous Graphene for Carbon Nanocircuitry	Oral	**27**
Filipe Almeida (i3N - CENIMAT, Portugal) Towards the development of dual-responsive composites for simultaneous hyperthermia and chemotherapy	Poster	**77**
Pedro Alpuim (INL, Portugal) High-quality graphene-based dispersions for flexible electronics	Invited	**21**
Iulia Antohe (National Institute for Laser, Plasma and Radiation Physics (INFLPR), Romania) Picomolar detection of 4-nitrophenol using a polyaniline/platinum - coated fiber optic surface plasmon resonance sensor	Oral	**28**
João Avó (Insituto Superior Técnico, Portugal) Nanomaterials with thermally-activated delayed fluorescence for live-cell imaging	Oral	**29**
Carlos Baleizão (Instituto Superior Técnico, Portugal) Smart hybrid silica nanocarriers with finely tuned structure for control release	Oral	**30**
Ana Isabel Barbosa (LAQV, REQUIMTE, FFUP, Portugal) Quercetin-loaded Hydrogels for Skin Ageing and Inflammation	Oral	**31**
Peter Bøggild (DTU Physics, Denmark) Synthesis and THz-characterisation of large-scale 2D materials	Keynote	**9**
Javier Bonet-Aleta (University of Zaragoza, Spain) Enzyme-mimicking catalytic Activity in Tumoral Microenvironment: Towards Glutathione-Glucose Depletion for Cancer Therapy	Oral	**32**
Francisco Brito (University of York, UK) Simulation of Quantum Spin-Liquid Phases with Spectral Methods	Oral	**33**
Diego Carvalho (Applied Molecular Biosciences Unit (UCIBIO), Portugal) Simple one-pot separation of histidine-tagged proteins using NTA-functionalized gold nanostars	FlashPoster	**68**
Flávia Castro (i3S, Portugal) Chitosan/γ-PGA nanoparticles-based immunotherapy as adjuvant to radiotherapy in breast cancer	Oral	**34**
Rute Chitas (i3S - Instituto de Investigação e Inovação em Saúde, Portugal) Optimization of drug-free nanostructured lipid carriers (NLC) for Helicobacter pylori eradication	FlashPoster	**69**
Wera Di Cianni (Università della Calabria/Universidad de Cadiz, Italia/Spain) Photoreduction: new strategies for Additive Manufacturing	FlashPoster	**70**
João Pedro dos Santos Pires (University of Porto, Portugal) From Positive to Negative Reflectance Response in Fibre Optics Tipped with Stacked Graphene/Dielectric Coatings	Oral	**35**
Cecílio Duarte (Instituto Superior Técnico, Portugal) Improving the mechanical performance of HDPE employing dendrimer-like silica nanospheres and halloysite natural nanotubes as promising nanofillers through in-situ polymerization	Poster	**78**
Khalil El Hajraoui (INL, Portugal) Scanning Transmission Electron Microscopy investigations of an efficiency enhanced annealed Cu(In1-xGax)Se2 solar cell with sputtered Zn(O,S) buffer layer	Oral	**36**
Maria Enea (University of Porto, Portugal) Synthesis, characterization and safety evaluation of gold nanoparticles	Oral	**37**
Xinliang Feng (TU Dresden, Germany) Advances in Organic 2D Materials	Keynote	**10**

Authors	Session	Page
Shlomo Magdassi (The Hebrew University of Jerusalem, Israel) Additive Manufacturing: the next industrial revolution	Keynote	**12**
Joao Mano (Universiy of Aveiro, Portugal) Nanotechnology approaches in the design of hybrid constructs for biomedicine	Keynote	**13**
Natércia Martins (University of Aveiro, Portugal) Composites of biopolymers and metal oxide nanoparticles for controlled release of micronutrients in agricultural soils	Oral	**48**
David Mecerreyes (Polymat, Spain) 3D Printable Conducting Polymers for Bioelectronics	Keynote	**14**
Duarte Moura (i3S - Instituto de Inovação e Investigação em Saúde, Universidade do Porto, Portugal) Biodegradable pHEMA containing graphene oxide for blood contacting applications	Oral	**49**
Edgar Muñoz (Instituto de Carboquímica ICB-CSIC, Spain) Supramolecular Two-Dimensional Peptidic Adhesives for Graphene Oxide Fiber Functionalization	Oral	**50**
Lili Nadaraia (Georgian Technical University, Georgia) The effect of graphene reinforcement on the properties of TiO$_2$	FlashPoster	**73**
Cláudia Nunes (LAQV, REQUIMTE, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal) Lipid based delivery systems design and development for inflammatory and infectious diseas	Invited	**24**
António Oliveira (International Iberian Nanotechnology Laboratory, Portugal) Novel rear structure design for an effective optical enhancement in ultrathin Cu(In,Ga)Se$_2$ solar cells	Oral	**51**
Maria João Oliveira (Centro de Investigação de Materiais - CENIMAT/i3N, Portugal) Sticky cellulose hydrogel as reusable a platform for a SERS based immunoassay	Oral	**52**
Evelyn Ospina (Universidad Politécnica de Madrid, Spain) New amperometric biosensor for determination of heavy metal ions based on the enzymatic inhibition of HRP immobilized on ferrocenyl polycyclosiloxane/Gold Nanoparticles modified electrode	Poster	**83**
Miguel Peixoto de Almeida (LAQV-REQUIMTE, Portugal) Silver Nanostar-based Biocide Surfaces	Poster	**84**
Vitor Pereira (NUS, Singapore) A novel canted spin Hall effect and spin-orbit torques in the 2D topological materials MoTe$_2$ and WTe$_2$	Keynote	**15**
Andreia Pereira (INEB, Portugal) Graphene: The key for pHEMA application as blood contacting devices	Oral	**53**
Nuno Peres (University of Minho, Portugal) Graphene Plasmonics	Keynote	**16**
Artur M. Pinto (LEPABE, Faculty of Engineering, University of Porto, Portugal) From nanographene production scale-up to its biomedical applications	Oral	**-**
Thais Priscilla Pivetta (CEFITEC, Faculty of Science and Technology, Universidade Nova de Lisboa, Portugal) Complex Liposomes for Phototherapy: development and optimization	Poster	**85**
Antonio Puente (Universitat de les Illes Balears (UIB), Spain) A Circular Model for Electron Configurations in 2D Heterostructures at High Magnetic Field	Poster	**86**
Agnes Purwidyantri (International Iberian Nanotechnology Laboratory, Portugal) Portable graphene transistor sensing system for wine DNA detection	Oral	**54**
Tiago Queirós (INL, Portugal) Oxygen assisted monocrystalline graphene growth by chemical vapor deposition	FlashPoster	**74**
Iran Rocha Segundo (University of Minho, Portugal) Modification of a transparent binder for road pavements using TiO$_2$ nanoparticles	Oral	**55**
João Rodrigues (International Iberian Nanotechnology, Portugal) Upscaling MoSe$_2$ and hBN via controlled chemical vapor deposition	FlashPoster	**75**

Abstracts Keynote

Synthesis and THz-characterisation of large-scale 2D materials

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Terahertz time-domain spectroscopy has developed into a powerful, versatile high throughput method for characterisation of the electronic properties of large-scale graphene. The absorption of terahertz radiation in the graphene layer directly links to the conductivity, and can reveal a number of key performance characteristics in far more non-invasive and convenient manner than conventional electronic measurements. By obtaining the full THz-spectrum in every point on a wafer or sheet of graphene, we shed new light on defects, imperfections, doping and grain structure, and even local variations in the Fermi velocity, which is particularly important for polymer substrates [2]. Due to graphene's high surface area, low carrier density and susceptibility to damage and contamination, high-quality metrology involves a number of challenges, which are important to understand. In the talk, I will overview the state of the art, highlighting learnings and accomplishments from the past few years of scientific collaborations on a variety of substrates and applications [3], and discuss what it will take to make THz-TDS conductivity mapping the golden standard of large-area graphene characterisation for wafer- and roll-to-roll production. I will also discuss some of our recent progress in large-scale graphene growth and transfer [4] and assembly of van der Waals heterostructures based on CVD materials [5].

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Advances in Organic 2D Materials

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In the past decade, as inspired by the discovery of graphene, two-dimensional (2D) materials which possess a periodic network structure and with a topographical thickness of atomic/molecular level, have emerged as the new paradigm of materials with enormous potentials, ranging from electronics and optoelectronics to energy technology, membrane, sensing and biomedical applications. Various synthesis/fabrication strategies have been developed to attain high quality 2D materials. Among of them, mechanical exfoliation remains the most popular protocol to isolate single-layer high quality 2D materials for fundamental physical studies.

In contrast to the tremendous efforts dedicated to exploring graphene and inorganic 2D materials such as metal dichalcogenides, boron nitride, black phosphorus, metal oxides and nitrides, the study on organic 2D material systems including the bottom-up organic/polymer synthesis of graphene nanoribbons, 2D metal-organic frameworks, 2D polymers/supramolecular polymers as well as supramolecular approach to 2D organic nanostructures remains under development. In this lecture, we will present our recent efforts on the bottom-up synthetic approaches towards novel crystalline organic 2D materials with structural control at the atomic/molecular-level. 2D conjugated polymers and coordination polymers thus belong to such materials classes. The unique structures with possible tailoring of conjugated building block and conjugation length, adjustable pore size and thickness, as well as interesting electronic structure make them highly promising for a number of applications in electronics and spintronics. Other application potential of organic 2D materials will be also discussed.

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Small metal clusters as efficient catalytic species with outstanding stability

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Transition metal clusters with a small number of atoms (≈ 2-10) are considered to be one of the most promising materials in catalysis, because they provide a way to avoid the limitations of both, traditional catalysts (lack of selectivity, cost and availability) and current single-atom catalysis (low degree of versatility to catalyse different kind of reactions) opening new ways to achieve better efficiencies and selectivity at low cost (see e.g. [1-4]).
One of the main concerns in the use of small metal clusters as catalysts is their stability. However, contrary to normal expectations, we have recently observed that small clusters posse outstanding chemical and thermal stabilities even with non-precious metals, such as copper [5]. We will report here details of such outstanding stabilities and some examples of catalytic activities with clusters synthesized by wet chemical procedures supported on oxides [6]. As an example, Figure 1 shows the catalytic aerobic oxidation of thiophenol to sulfone by Ag clusters of 5 atoms at ambient conditions, showing the potential of such clusters for the room temperature aerobic desulfurization of petrol.

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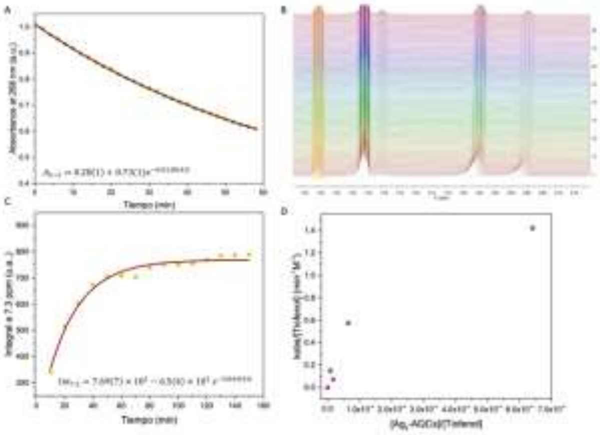

Figure 1: Time evolution for the aerobic oxidation of thiophenol catalyzed by Ag_5 clusters (Ag_5-AQCs). A) Absorbance disappeared at 268 nm (diphenyl disulfide) with time for a thiophenol solution of 1 mM with molar ratio 6.4 x 10^{-4} and the adjustment to an exponential function. B) Proton spectra evolution time for a 15 mM thiophenol solution with a molar ratio with AQCs of 1 x 10^{-5}. C) Integral at 7.5 ppm versus time for the reaction described in B. D) Observed kinetic constant versus the concentration of Ag_5-AQCs both divided by the concentration of thiophenol.

Additive Manufacturing: the next industrial revolution

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Abstract

Additive manufacturing which is based on printing processes, is considered as the next industrial revolution. Functional printing brings additional performance of printed patterns, beyond the conventional graphic output. The synthesis and formulations of nanomaterials and inks will be presented, with their utilization in printed devices, responsive and 3D objects. New approaches for achieving conductive inks for printed plastic electronics will be presented, as well as new materials and processes for 3D and 4D printing. Utilization of 3D and 4D printing technologies for fabrication of objects composed of ceramics, shape memory polymers, elastomers and hydrogels will be demonstrated, for applications such as soft robotics, drug delivery systems, responsive connectors and Internet of Things (IoT), dynamic jewellery and medical devices.

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Nanotechnology approaches in the design of hybrid constructs for biomedicine

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In Regenerative Medicine, Tissue Engineering has been integrating principles of engineering, chemistry, materials science, biology and health sciences in order to develop regenerative-based therapeutic strategies combining stem cells and biomaterials. The development of hybrid devices for tissue engineering are often inspired by the composition and complexity of native tissues. At the lowest level of such organization, one should select the adequate biomaterials to be used as the building block of the structure that will support cells and control their behaviour towards the production of new tissue. Nanostructured multilayered films have been often fabricated using the layer-by-layer technology, where consecutive layers of macromolecules are well stabilized by electrostatic interactions or other weak forces. Such multilayered could be then integrated in more complex porous macroscopic devices, often exhibiting a multi-scale organization. Using adequate templates, non-flat multilayers can be fabricated with tuned compositions along the build-up assembly, including patterned membranes or porous devices. This enables the production of very well controlled multifunctional and structural devices using mild processing conditions that could be useful in biomedicine, including in tissue engineering. In particular, we have been interested in developing more complex/hierarchical porous structures using natural-based polymers that could fulfil specific requirements in such kind of applications. Methodologies developed in our group will be exemplified, permitting the production of (i) 3-dimensional (open) porous nanostructured scaffolds for tissue engineering, enabling the support of cells, by combining LbL and rapid prototyping technology; and (ii) free-standing films featuring patterns to control cell orientation or micro-wells to provide local three-dimensional environments to the cells.

3D Printable Conducting Polymers for Bioelectronics

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Ionic and electronic conducting polymers are searched in the area of bioelectronics for the development of innovative medical devices. The design of artificial scaffolds and devices which interact with the human body relies on the ability to control the mechanical and electrical signals, together with the material composition, topography and biocompatibility. New medical devices such as bioresponsive electrodes, biosensors, electronic skin and neural or muscle regeneration show the need of new conductive materials that can be printed. In this presentation we will show the recent activities carried out within the IONBIKE RISE project (www.ionbike-rise.eu) towards the development of printable conducting polymers. The presentation will include different materials and additive manufacturing methods based on the use of light or temperature such as:

- 3D printing of supramolecular iongels by Fused Deposition Modelling
- 3D printing of conducting PEDOT hydrogels by Stereolithography
- 3D printing of biodegradable and conducting PEDOT/PLA polymers by FFF

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FIGURES

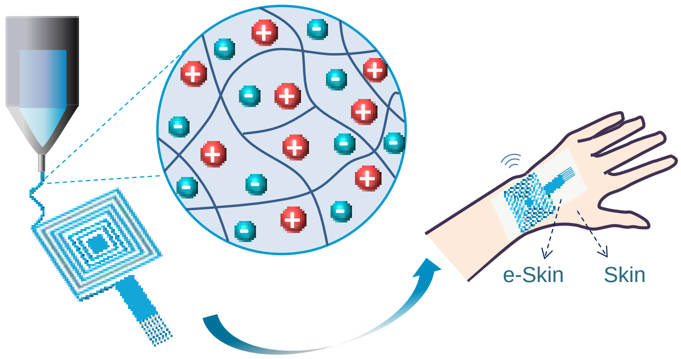

Figure 1: Schematic representation of printing of a conducting polymer for e-skin applications

A novel canted spin Hall effect and spin-orbit torques in the 2D topological materials MoTe2 and WTe2

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ABSTRACT

The field of spintronics has evolved tremendously beyond its founding concepts of giant and tunnel magnetorresistances that dominated research in the 1990's and early 2000's. The discovery, understanding and manipulation of new effects such as the spin Hall effect (SHE), the quantum SHE and spin-orbit torques, remarkably widened the toolbox of microscopic mechanisms and material platforms available to manipulate and optimize spin transport towards more effective, low-power information processing and storage technologies. I will present the most recent new direction brought about by combining two-dimensional topological materials, reduced symmetries and strong spin-orbit coupling: the canted (quantum) spin Hall effect. I will overview recent experimental and theoretical work [1-3] where we establish that a family of transition-metal dichalcogenides — which includes WTe2 and MoTe2 — displays the first realization of a canted SHE, and is accompanied by a set of other unique — and highly desirable — spintronic characteristics: extremely long spin diffusion lengths, persistent spin textures, and gate-tunable SHE. The underlying physics will be discussed based on a microscopic model that has been developed from first-principles and validated through extensive numerical simulations of spin transport and the SHE in these materials. I will also show theoretical and experimental work that, in addition, demonstrates the promising potential of these systems for nonlinear magnetotransport [4] and, in particular, to generate large and gate-tunable spin torques [5], thereby enabling all-electrical magnetization switching using atomically-thin semiconductor materials; in a proof-of-principle experiment, we demonstrate their effectiveness in reducing critical switching currents.

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Graphene Plasmonics

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In this talk we introduce the basic notions of graphene plasmonics. We discuss two important systems: graphene on a metallic grating and metallic nano-cubes dispersed on graphene. In both cases acoustic plasmons can be excited by far field mid-IR electromagnetic radiation. The role of non-local effects in the metallic pillars is also analysed.

The new generation of nanomedicines for biomedical applications: Dressing nanoparticles in cell's clothing

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The recent cutting-edge advances on nanomaterials is anticipated to overcome some of the therapeutic window and clinical applicability of many drug/peptide molecules and can also act as innovative theranostic platform and tool for the clinic in the future [1-4]. In the last decade, research on cancer immunotherapy resulted in a new set of potential treatments with promising results in the clinics[5-8]. Among these, immune checkpoint inhibitors are one of the few immunotherapies that have been clinically validated, yet with variable results, ranging from complete responses to hyperprogression. Amongst the different experimental treatments, active cancer immunotherapy hold great promises for the future. In this work, prominent nanosystems, such as biohybrid nanocomposites made of different nanoparticles (porous silicon and oncolytic virus) and cancer cell-based membrane materials are presented and discussed as potential platforms for the individualization of medical intervention and cancer immunotherapy applications. Examples on how these biohybrid nanomaterials can be prepared and scaled-up, as well as how they can be used to enhance the drug's targetability, intracellular drug delivery for both cancer chemo- and immune-therapy applications, will be highlighted and discussed. Overall, our results suggest that biohybrid nanomaterials are a versatile and advanced platform for cancer treatment with an interesting potential for present and future clinical impact given its easy tailorability to each patient, choosing a suitable inorganic or virus and obtaining cancer cells from biopsy.

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Targeting pancreatic tumors with nanomedicine

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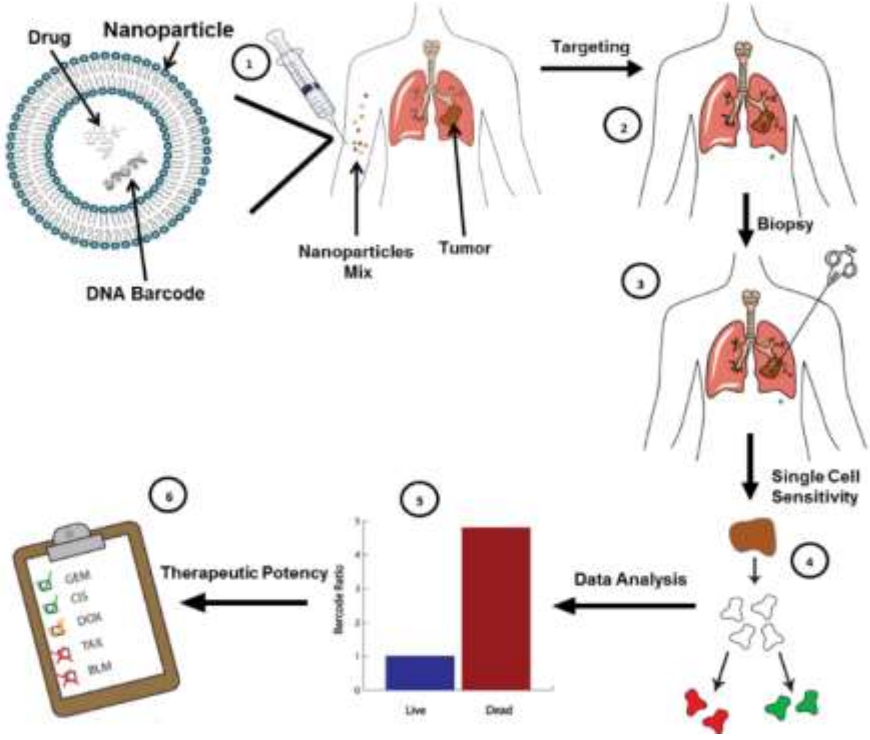
Medicine is taking its first steps towards patient-specific cancer care. Nanoparticles have many potential benefits for treating cancer, including the ability to transport complex molecular cargoes including siRNA and protein, as well as targeting to specific cell populations.

The talk will discuss ‘barcoded nanoparticles’ that target sites of cancer where they perform a programmed therapeutic task. Specifically, liposomes that diagnose the tumor and metastasis for their sensitivity to different medications, providing patient-specific drug activity information that can be used to improve the medication choice.

The talk will also describe how the liposomal lipid composition are used as multi-functional systems for degrading the pancreatic stroma to allow subsequent drug penetration into pancreatic adenocarcinoma, and how the nanoparticle configuration can be leveraged to induce an anti-tumor immune response.

The evolution of drug delivery systems into *synthetic cells*, programmed nanoparticles that have an autonomous capacity to synthesize diagnostic and therapeutic proteins inside the body, and their promise for treating cancer and immunotherapy, will be discussed.



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Graphene plasmonics with a drift-current bias

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Abstract

We will present an overview of our recent work on plasmonics in a drift-current biased graphene platform [1]-[4]. We will show that such a system provides a novel route to break the time-reversal symmetry and achieve strong nonreciprocal responses at the nanoscale. Our theoretical and numerical studies demonstrate that the biasing of a graphene sheet with a drift electric current enables the propagation of unidirectional surface plasmons and originates a highly asymmetric electron energy loss spectrum. Furthermore, it will be highlighted that a drift-current biased graphene system is an active system. In particular, it will be shown that by coupling the drift-current biased graphene sheet to another plasmonic slab (e.g., a semiconductor slab), it is possible to obtain regimes of negative Landau damping wherein the surface plasmons are pumped by the drifting electrons.

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FIGURES

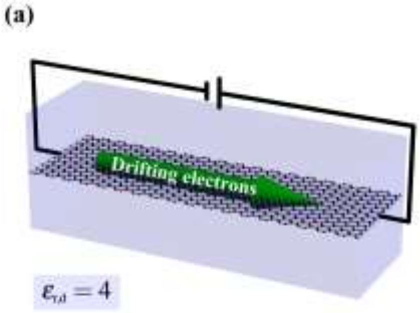

Figure 1: Sketch of a graphene sheet biased with an electric drift current.

Abstracts Invited

High-quality graphene-based dispersions for flexible electronics

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Abstract

The development of graphene-based nanomaterials for flexible electronics is of high interest for the industry [1]. Graphene-based liquid dispersions are suitable for the deposition of films with high electrical conductivity, transparency, and flexibility at low cost that are compatible with a wide range of substrates [2,3]. To date, graphene dispersions present some limitations, in particular the use of efficient, yet hazardous solvents with limited substrate compatibility, high boiling point and toxicity, which are all undesirable features for industrial production. We propose a novel approach to produce graphene-based dispersions with high yield and control on the material properties. By using a combination of shear mixing and ultra-sonication with tuned conditions (such as time, frequency, and power), we obtained stable graphene dispersions with concentrations above 4 mg/mL (with lateral size of the graphene flakes between 30 and 500 nm, fig.1). The dispersions can then be deposited by several techniques (e.g., spray coating, inkjet and screen-printing, etc.) on various substrates to fabricate films with desired levels of transparency and conductivity. In our tests, specific formulations for spray coating were prepared by mixing the graphene-based dispersions with polymeric additives. These formulations were used to spray-coat films on flexible PET and glass substrates, achieving an optical transmission (in the visible range) of 70-91% and a sheet resistance of 0.35-4 kΩ/□. An essential contribution towards the use of graphene inks is provided in this work by the use of a new green carbon solvent – Cyrene, which was able to replace toxic and hazardous solvents such as NMP and DMP in the exfoliation process, and allowed to produce highly concentrated and stable graphene-based dispersions with a very narrow distribution of graphene flake sizes.

As a proof of concept, a 20x20 channel multi-touch screen prototype was successfully fabricated on PET by spray coating our graphene ink through polymeric masks cut in a microplotter (see fig.1). Silver inks were prepared for the contacts, providing electrical connection to the graphene sense channels. PET films were treated in plasma for 5 sec to improve the wettability and adhesion.

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FIGURES

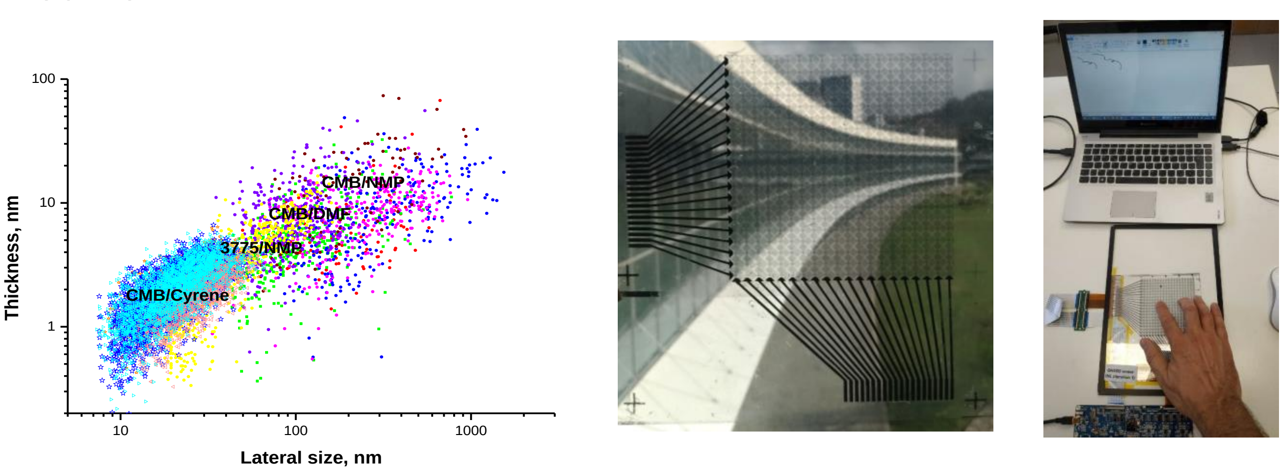

Figure 1: (left) AFM study of graphene flakes selected from their dispersions in different solvents (NMP, DMP, Cyrene); (center and right) graphene 20x20 channel multi-touch screen fabricated on PET.

Nanotechnological approaches for immune modulation against solid cancers

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Abstract

Despite the remarkable efficiency of cancer immunotherapies, only a low percentage of patients achieve long lasting clinical responses. Non-tumor cells within the tumor microenvironment (TME), including tumor vasculature and immune stromal cells, dictate the overall therapeutic efficacy[1].

We developed nano-sized medicines to re-educate and harness patient immune responses against tumors, yielding an immunological memory able to control tumor relapse without any follow-up treatment.

Nanomaterials were synthesized[2] to co-incorporate tumor-associated antigens, clinically relevant toll-like receptor ligands and regulators of tumor-related pathways, namely immune checkpoints, and cytokines. Nanoparticle (NP) physico-chemical properties were fully addressed. The immunotherapeutic potential of our multifunctional nano-based vaccines was assessed *in vivo* in melanoma (B16F10, B16-OVA), MC38 colorectal cancer (CRC) and 4T1 triple negative breast cancer (TNBC) mouse models, isolated and in combination with modulators of immune checkpoint function and cytokine secretion. We evaluated tumor volume, survival, and characterized the TME-infiltrating immune cells.

Our nanovaccine remodeled the TME and sensitized melanoma, CRC, and TNBC to immune checkpoint therapy, significantly delaying tumor development and increasing disease-free survival rates. These nano-based immunotherapies led to the induction of a broad effector and memory anti-tumor immune response, demonstrating that our new nanovaccine constitutes a promising immunotherapy clinically translatable to defeat solid tumors.

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Exploring Graphene for Biomedical Applications: a strong ally for hydrogels and a sharp enemy for bacteria

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Abstract

Thrombosis and infection are the major problems associated with blood contact devices. Making use of graphene based materials (GBMs) outstanding mechanical strength and high area/thickness ratio, and by playing with GBM thickness, lateral size and oxidation degree, it is possible to design novel biomaterials with antibacterial, bio/hemocompatible and mechanically suitable properties. We have explored different conjugations of GBMs, polymers/matrices and production techniques according to the desired application [1]. GBM-containing biomaterials were designed towards two main biomedical applications: i) as antimicrobial composites and coatings for dialysis catheters [2-5]; and ii) mechanically reinforced hydrogels for vascular grafts [6]. Results highlight the importance of GBM exposure on the surface of the biomaterials in order to exert antimicrobial properties, with oxidized GBMs presenting better performance. The oxidation degree also seems to be a detrimental factor in the mechanical reinforcement of hydrogels. Poly(2-hydroxyethyl methacrylate) (pHEMA)/ graphene oxide composites stand out as biomaterial with antibacterial and anti-thrombogenic properties, revealing huge potential for load-bearing applications, including blood contact devices.

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Lipid based delivery systems design and development for inflammatory and infectious diseases

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The pharmaceutical research is increasingly linked to nanotechnology, due to the remarkable characteristics of nanoscale vectors for drug delivery. Among the multiple approaches, lipid based nanoparticles are considered the most promising since they are composed by highly biocompatible molecules and may enable site-specific release of bioactive compounds due to their high stability, high carrier capacity and ability to load both hydrophilic and hydrophobic substances.

In this presentation, two examples of these types of nanoparticles as drug delivery systems will be discussed. Emphasis will be given to the rational design, focused on nanoparticles features, the physico-chemical properties of the encapsulated bioactive compounds, the target microenvironment and how the three should guide formulation choices. Simultaneously, key characterization procedures and *in vitro* interaction studies will be pointed out.

The first study describes hyaluronic acid-conjugated pH-sensitive liposomes as an effective drug delivery-targeting strategy to synovial cells [1]. Overall, results reveal that conjugated pH-sensitive liposomes are a promising nanoapproach for the targeted delivery of prednisolone within inflamed synovial cells for rheumatoid arthritis treatment.

The second study addresses the encapsulation of amoxicillin in lipid nanoparticles, increasing the retention time at the site of infection (gastric mucosa), while protecting the drug from the harsh conditions of the stomach lumen [2]. Overall, the designed formulations present suitable physico-chemical features for being henceforward used by oral administration to treat *Helicobacter pylori infections* (figure 1).

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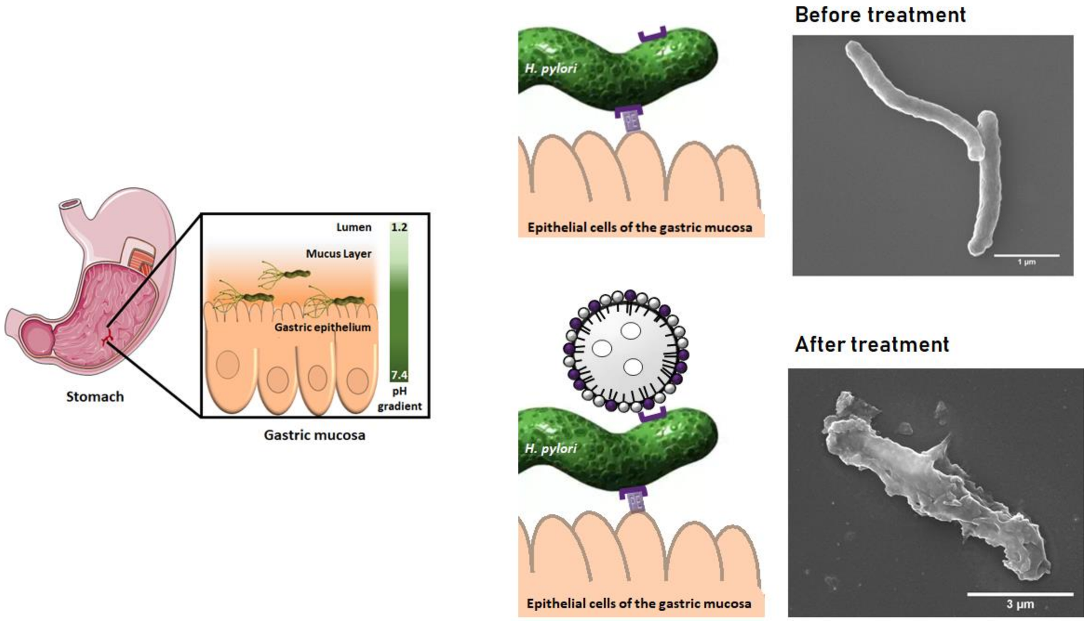

Figure 1: Lipid nanoparticles strategy to target *Helicobacter pylori*.

Graphene-based material platforms for quantum and terahertz nonlinear technologies

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One of the many interesting properties of graphene is that it can be integrated into hybrid structures, where graphene is in atomically close proximity to other material systems. This property can be exploited to open up novel device capabilities. This talk will discuss two recently demonstrated implementations of such novel hybrid material platforms based on graphene – one with relevance for quantum technology; and one relevant for nonlinear signal processing.

The first hybrid material platform consists of a nanolayer of erbium emitters (~10 nm thick) in direct contact with a gate-tunable monolayer of graphene [1]. This system thus combines the optical addressability of erbium ions with high-speed, all-electrical modulation of the strong near-field interactions between the emitters and graphene. Modulation is made possible via both a *p*-doped silicon backgate and a polymer electrolyte topgate. In this hybrid erbium-graphene system, we observe a significant fraction of erbium ions with a decay rate that is enhanced by a factor 1,000 and higher due to strong dipole-dipole interaction with graphene. This indicates that extremely efficient emitter-graphene interaction occurs: 99.9% of the energy of these excited erbium emitters flows to graphene. The energy that is transferred from excited erbium emitters to graphene leads to either electron-hole pair generation or plasmon launching in graphene, depending on the Fermi energy of graphene [2]. By rapidly modulating the gate voltage of only a few Volt, we modulate the energy flow path, and thereby the emitter-graphene interaction strength. Interestingly, we demonstrate modulation with a frequency up to 300 kHz, many orders of magnitude faster than the natural decay rate of erbium ions of ~100 Hz. This constitutes an enabling platform for integrated quantum technologies, for example opening routes to quantum entanglement generation by collective plasmon emission or photon emission with controlled waveform.

In the second hybrid material platform, we combine monolayer graphene with a metallic grating. Exploiting the grating-induced field enhancement, this hybrid grating-graphene metamaterial leads to a strongly increased optical nonlinearity in the terahertz range [3], which was already very large for bare graphene [4]. We find an unprecedently large third order (sheet) susceptibility in the terahertz range of tens of ESU, equivalent to $>10^{-8}$ m^2/V^2. Moreover, we observe terahertz (THz) third-harmonic generation with a field conversion efficiency above 1%, and 9th harmonic generation, both with a very moderate field strength of tens of kV/cm. This is remarkable, since nonlinear optics typically requires field strengths in the MV/cm range, thus enabling much lower power consumption. This hybrid grating-graphene metamaterial system is thus highly promising for on-chip nonlinear signal processing in the THz.

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Abstracts Oral

Quantum Interference Engineering of Nanoporous Graphene for Carbon Nanocircuitry

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Bottom-up prepared carbon nanostructures appear as promising platforms for future carbon-based nanoelectronics due to their atomically precise and versatile structure.**[1]** An important breakthrough is the recent preparation of nanoporous graphene (NPG) as an ordered covalent array of graphene nanoribbons (GNRs, **Figure 1a**).**[2]** Within NPG, the GNRs may be thought of as 1D electronic nanochannels through which electrons preferentially move, highlighting NPG's potential for carbon nanocircuitry. However, the π-conjugated bonds bridging the GNRs give rise to electronic crosstalk between the individual 1D channels, leading to spatially dispersing electronic currents (**Figure 1b**).**[3]** In this talk, we propose a chemical design of the bridges resulting in destructive quantum interference (QI), which blocks the crosstalk between GNRs in NPG, electronically isolating them. Our multiscale calculations reveal that injected currents can remain confined within a single, 0.7 nm wide, GNR channel for distances as long as 100 nm (**Figure 1c**).**[4]** The concepts developed in this work thus provide an important ingredient for the quantum design of future carbon nanocircuitry. In addition, our latest results demonstrating an external control of these characteristics will also be presented.

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FIGURES

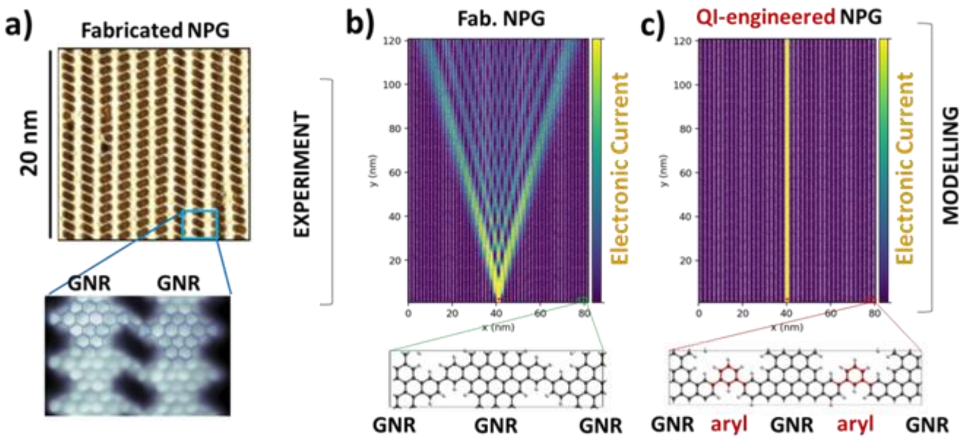

Figure 1: (a) Scanning tunneling microscopy image of the fabricated NPG. Inset: high-resolution image of the 2D material; **(b)** Electrical injection simulation in a large-scale model of the fabricated NPG and **(c)** in our proposed QI-engineered NPG.

Picomolar detection of 4-nitrophenol using a polyaniline/platinum - coated fiber optic surface plasmon resonance sensor

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Fiber Optic – Surface Plasmon Resonance (FO-SPR) technology has been recognized as a remarkable optical sensing tool in various fields of life science, agro-food sector and medical diagnostics, as it can provide efficient characterization and real-time quantification of various biological entities [1]. Potential applications can span from studying interactions between proteins, lipids, nucleic acids, to even low molecular weight molecules such as drugs [2-3].

Herein, we present an innovative polyaniline (PANI)/platinum (Pt)-coated fiber optic – surface plasmon resonance (FO-SPR) sensor (see Figure 1) used for highly-sensitive 4-nitrophenol (4-NP) pollutant detection. The Pt thin film was coated over an unclad core of an optical fiber (FO) using a DC magnetron sputtering technique, while the 4-NP responsive PANI layer was synthetized using a cost-effective electroless polymerization method. The presence of the electrolessly-grown PANI on the Pt-coated FO was observed by field-emission scanning electron microscopy (FE-SEM) and subsequently evidenced by energy dispersive X-ray analysis (EDX). These FO-SPR sensors with a demonstrated sensitivity of 1515 nm/RIU were then employed for 4-NP sensing, exhibiting a promising limit of detection (LOD) in the low picomolar range (0.17 pM). The proposed sensor's configuration has many other advantages, such as low-cost production, small size, immunity to electromagnetic interferences, remote sensing capability, and moreover, can be operated as a "stand-alone device", making it thus well-suited for applications such as "on-site" screening of extremely low-level trace pollutants.

This work was supported by the "Executive Unit for Financing Higher Education, Research, Development and Innovation" - UEFISCDI (Romania) through the grants PN-III-P1-1.1-PD-2019-0466 and PN-III-P1-1.1-TE-2019-0868, the National Authority for Research and Innovation in the frame of Nucleus Programme - LAPLAS VI (contract 16N/08.02.2019) and by the University of Bucharest, Faculty of Physics through a doctoral scholarship.

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FIGURES

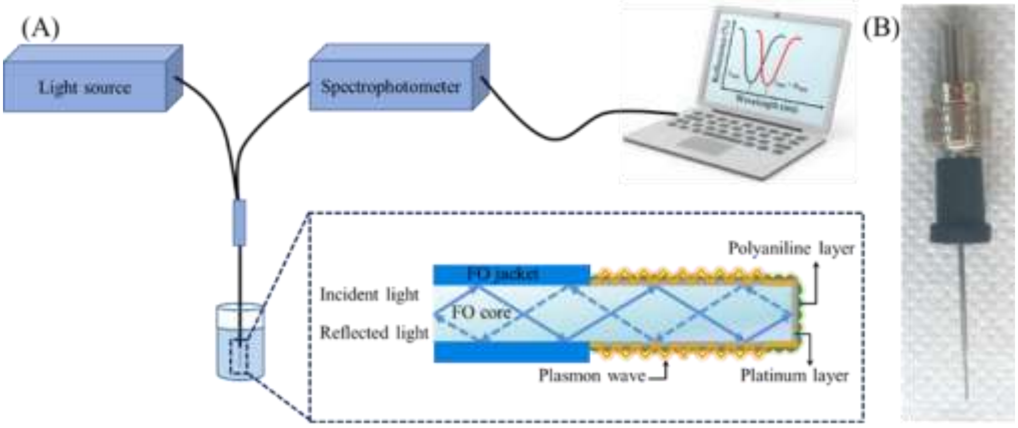

Figure 1: Schematic of the FO-SPR setup (A) and a picture of the fabricated Pt-coated FO-SPR sensor (B).

Nanomaterials with thermally-activated delayed fluorescence for live-cell imaging

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Thermally activated Delayed Fluorescence (TADF) has recently revolutionized the field of OLEDs owing to the ability of harvesting energy from non-emissive triplet states. This mechanism generates a long-lived photoluminescence component that also has tremendous potential to be used in optical sensing of local oxygen concentration and temperature or in time-resolved optical imaging.[1] Despite this strong potential, the application of TADF molecules in imaging and sensing has been hindered thus far due to their low aqueous solubility, low biocompatibility and poor performance in polar media.[1-3] Here in we demonstrate an approach to attain TADF luminescence in water, based on the encapsulation of TADF dyes in nanoparticles that effectively preserves their optical properties. Our luminescent nanoparticles were evaluated as potential optical probes for optical imaging, showing excellent biocompatibility and good cellular uptake. After effective internalization by human cancer cells, the luminescent nanoparticles localize primarily in the cytosol, enabling fluorescence microscopy imaging at very low dye concentrations.[2,3]

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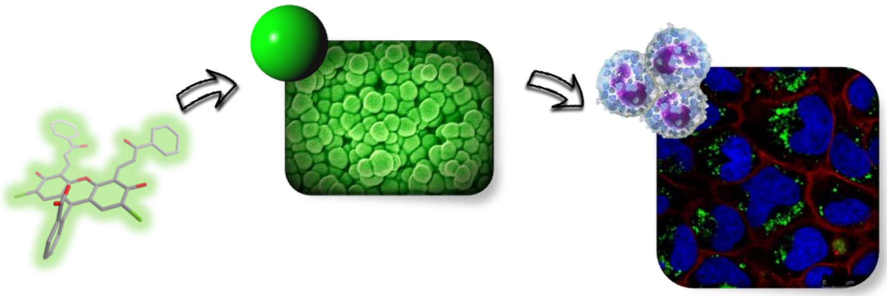

Figure 1: A TADF fluorescein derivative is grafted onto silica nanoparticles and used as TADF emitting optical probe in fluorescence imaging of cancer cells

Smart hybrid silica nanocarriers with finely tuned structure for control release

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Mesoporous silica nanoparticles (MSNs) have been used in theranostic applications as nanocarriers in cutting-edge applications due to their excellent biocompatibility, high surface areas, large pore volumes, high loading capacity, uniform and tunable pore sizes, and versatile surface functionalization [1]. This synthetic versatility allow i) the incorporation of fluorescent dyes into the silica structure yielding hybrid nanomaterials with excellent optical properties for imaging [2]; ii) the modification of the external surface with biomolecules for active targeting [3]; and iii) coating of the external surface with stimuli-responsive polymers for delivery control [4]. One important challenge remaining in their preparation is the ability to tune their diameter in the range of a few tens of nanometers, with narrow size dispersity, preferably using a simple and sustainable process.

In this communication we will start by presenting a fully controllable low-temperature and purely aqueous sol-gel method to prepare MSNs with user-defined diameters from 15 nm to 80 nm and narrow size dispersity [5-6]. The method also allows modification of the pore structure and offers the possibility of incorporating a luminescent species in the silica network for optical traceability. Control was achieved by tuning the colloidal stability of the assembly of cylindrical micelles that template the MSN synthesis. Using CTAB cylindrical micelles as template and NaOH as catalyst, precise diameter control was achieved either by changing the pH (that controls micelle surface charge) or by adding ionic compounds at constant pH (to tune the ionic strength and charge screening). The specific interactions of salts counterions with surfactant head groups affect their self-assembly properties through intra- and intermolecular forces, and we have rationalized these results based on the Hofmeister series.

We will show how MSNs modified at the external surface with a polymer shell featuring conformational changes induced by pH [7-8] or temperature [9], can act as precise gate keepers to control cargo release from the MSNs pore system. The nanoparticles feature either a polymer brush or a gel-like responsive shell, produced by grafting from RAFT polymerization that offers low size dispersity and well-defined end-groups. Additionally, the internal surface was modified to interact preferentially with the cargo to improve decrease leakage in the “off” release state. These new methodologies open a new path for the use of hybrid polymer-shell MSNs in theranostics.

This work was partially supported by FCT-Portugal and COMPETE/FEDER, projects UIDB/00100/2020, UIDP/00100/2020 and PTDC/CTM-CTM/32444/2017.

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Quercetin-loaded Hydrogels for Skin Ageing and Inflammation

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Nature has led to the discovery of interesting compounds, with noteworthy applications in nanotherapeutics. Particularly from the marine environment, sodium alginate (SA) is a marine polymer that demonstrated the ability to form hydrogels, an interesting property for the development of cutaneous nanoformulations [1]. SA is commonly combined with other polymers to attain specific hydrogel properties; such it is the case of poly(vinyl) alcohol (PVA). In fact, hydrogels have been gaining interest among research groups for cutaneous application instead of other conventional dosage forms (creams, lotions, ointments), and the main advantages are related with higher water content and non-greasy texture, better skin feel and cooling effect, better skin hydration and longer drug absorption, reduced transepidermal water loss, skin biocompatibility and better patient compliance [2, 3]. Quercetin, a natural polyphenolic flavonoid commonly found in fruits and vegetables, is widely known for its strong anti-inflammatory and antioxidant activity. Particularly in skin research, quercetin was reported as active against melanoma, inflammation, and skin ageing [4].

In this work, the potential of quercetin-loaded SA/ PVA hydrogels was explored as a non-invasive nanostrategy to overcome skin inflammatory diseases and skin ageing. To explore the combination of these two polymers, 3 different SA/ PVA blended hydrogel ratios were prepared (1:1, 2:1 and 1:2) and the same combinations were formulated to incorporate quercetin in its structure, proceeding to its physicochemical characterization and skin permeation profile.

The designed hydrogels were found to have pH around 6, which is adequate to for skin application, and revealed a quercetin entrapment efficiency of 60%. Complementary analysis of swelling assay was performed for 3 hours, concluding that the higher amount of sodium alginate in the hydrogel leaded to a higher swelling capacity. All hydrogels were analysed by Fourier-transformed Infrared Spectroscopy, morphological analysis was performed by Scanning Electron Microscopy, as well as elemental analysis by Energy-dispersive X-ray spectroscopy. Aiming the cutaneous application of the formulations, all unloaded and quercetin-loaded hydrogels were submitted to rheology studies. The main observations revealed pseudoplastic behaviour, no evidence of thixotropy, good resistance to deformation and profile maintenance with temperatures ranging from 20°C up to 40°C. Quercetin loaded SA/ PVA blended hydrogel exhibited antioxidant activity, confirmed by radical scavenging assays (ABTS and DPPH).

To evaluate the penetration/ permeation of quercetin through the skin, two different models were used: the Human *stratum corneum* Phospholipid Vesicle-based Permeation Assay and the isolated *stratum corneum* from pig ear skin. Both model barriers revealed high penetration and low permeation of the flavonoid at the end of 24 hours. This behaviour will allow a local and prolonged skin effect, making the use of these hydrogels a good solution to consider for the treatment of skin ageing and inflammation.

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Enzyme-mimicking catalytic Activity in Tumoral Microenvironment: Towards Glutathione-Glucose Depletion for Cancer Therapy

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New strategies in cancer therapy focus on the degradation of key metabolites, such as Glutathione (GSH) [(1)] or Glucose [(2),(3)]. GSH is a natural antioxidant which maintains the cytosol concentration of Reactive Oxygen Species (ROS) (e.g. H_2O_2, O_2^- or $^{\cdot}OH$) below cytotoxic levels. Since glucose is the major source of energy in cells, particularly under neoplasia, large amounts of this metabolite are required to ensure ATP levels. Thus, new nanomaterials showing the ability to alter these molecules levels (Figure 1) may have an effect on controlling cancer growth. In this work, synthesis and characterization of a nanoplatform based on Cu(II) and Fe(III) with outstanding enzyme-like activity mimicking towards GSH-oxidation are presented. As cytosol GSH levels decrease, more H_2O_2 is available to increase ·OH hydroxyl levels via Fenton-process. High reactivity of ·OH radicals is responsible for oxidizing glucose, DNA, amino acids or membrane-lipids, causing critical cell damage entailing cell apoptosis. In this way, the catalytic peroxidation of organic molecules is enhanced in the presence of GSH.

A spinel-like Cu(II)Fe(III) mixed nanoxide with additional NIR response has been synthesized. Its catalytic activity in tumoral-like conditions (i.e. high GSH/H_2O_2 levels and mildly-acidic pH) was higher in comparison with non-GSH conditions. Moreover, their metabolic cytotoxicity and its internalization mechanism within two different cell lines (U-251MG and hpMSC) were evaluated in order to achieve a deeper understanding in their interaction with different cells.

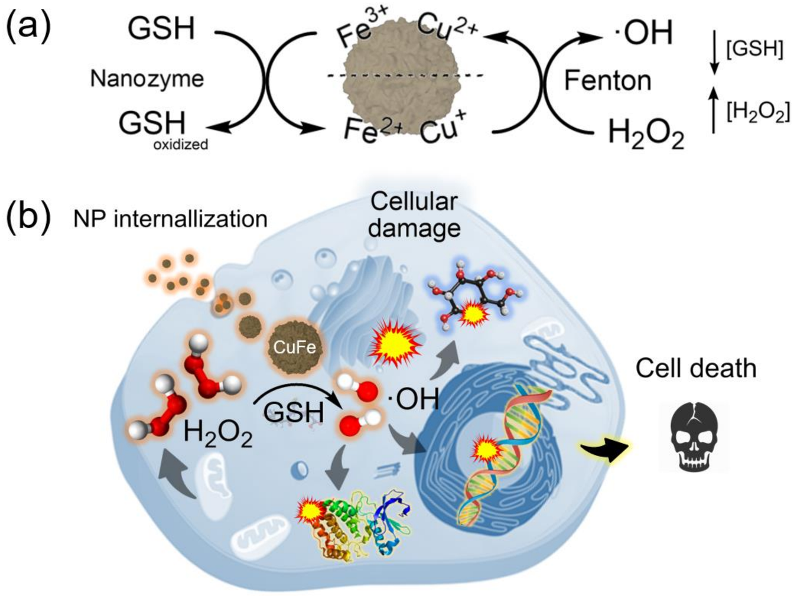

Figure 1. Schematic view of CuFe action mechanism. (a) Dual activity of CuFe catalyst: its interaction with tumour-abundant GSH enhances the generation of toxic ·OH radicals, which (b) can damage key compounds in cells such as glucose, DNA and proteins, entailing cell death.

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Simulation of Quantum Spin-Liquid Phases with Spectral Methods

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Abstract

In this work, we combine accurate Chebyshev polynomial expansions [1, 2] and thermal pure quantum states (TPQ) [3] to simulate quantum spin models with highly entangled ground states. We use this hybrid framework to map out in a numerically exact fashion the phase diagram of the Kitaev-Heisenberg model on the honeycomb lattice [4]; see Figure 1. Energy, magnetization and spin correlations are calculated with spectral accuracy in large systems with up to 24 spins. Our method can be easily extended to realistic spin models accommodating impurities, defects and external perturbations. Our results suggest that the hybrid spectral-TPQ approach can provide advantages over pure TPQ and other state-of-the-art methods in probing complex spin systems.

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FIGURES

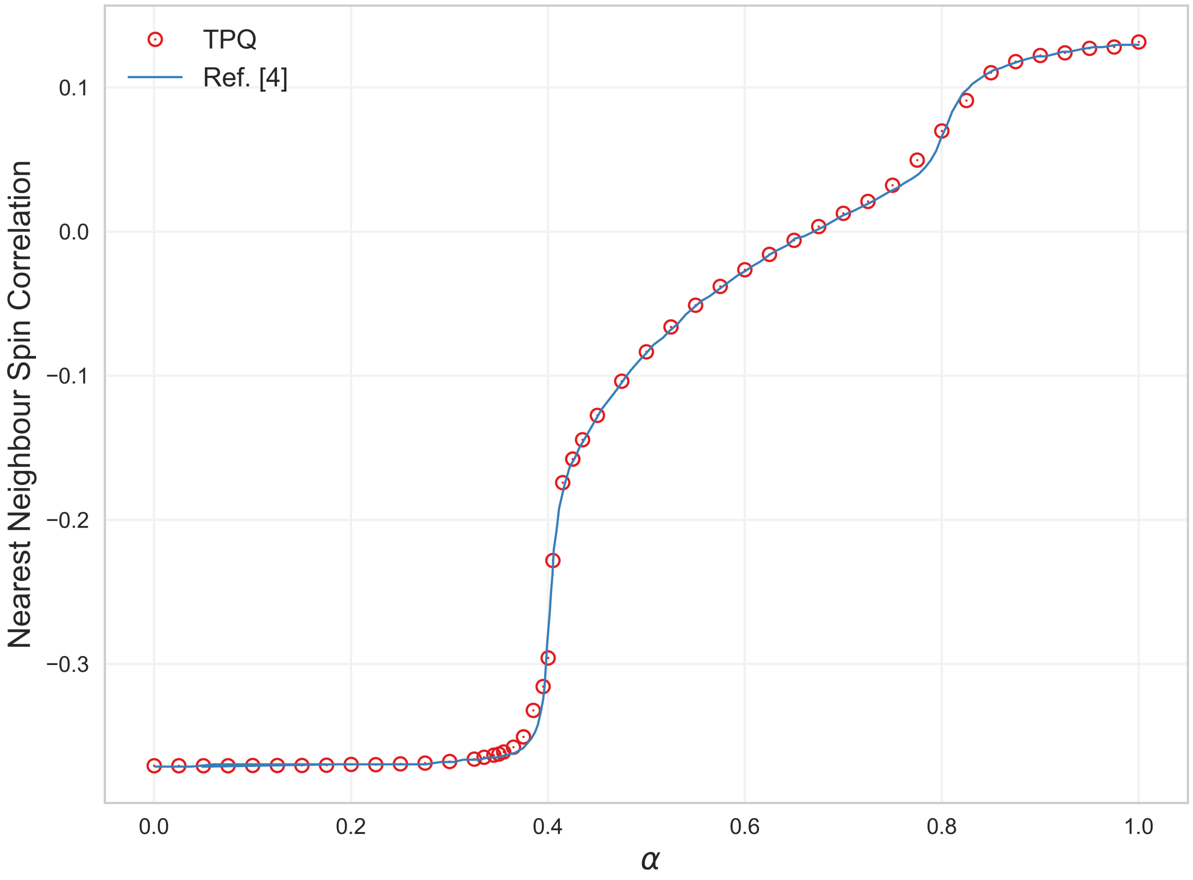

Figure 1: Spin-spin correlations for nearest neighbours for the Kitaev-Heisenberg model on a honeycomb lattice with 24 sites. Here, α is a parameter that interpolates between the Heisenberg and Kitaev models. For $\alpha = 0$, we have the Heisenberg model and for $\alpha = 1$, we have the Kitaev model, which is exactly solvable.

Chitosan/γ-PGA nanoparticles-based immunotherapy as adjuvant to radiotherapy in breast cancer

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Radiotherapy (RT) is an essential treatment modality for several types of cancer. Despite its therapeutic potential, RT is frequently insufficient to overcome the immunosuppressive nature of the tumor microenvironment, failing to control tumor metastases. Innovative immunomodulatory strategies, like immunostimulatory biomaterials could be used to boost the immunogenic effects of RT. We have reported that chitosan (Ch)/poly(γ-glutamic acid) (γ-PGA) nanoparticles (NPs) modulate immature/immunosuppressive APCs, namely macrophages and dendritic cells, towards an immunostimulatory profile, impairing their ability to induce cancer cell invasion [1]. Furthermore, Ch/γ-PGA NPs have also been shown to be potential carriers for immunomodulatory drugs, such as interferon (IFN)-γ [2].

Herein, we addressed the synergistic potential of immunostimulatory chitosan/poly(γ-glutamic acid) nanoparticles (Ch/γ-PGA NPs) [1] combined with RT to induce antitumor immunity in the 4T1 breast tumor mouse model. Therefore, animals were divided in 4 groups: non-treated, treated with NPs, with RT or with NPs+RT. Briefly, 4T1 cells were injected orthotopically in BALB/cByJ. After 7 days, animals from RT and RT+NPs groups were locally irradiated with hypofractionated 10Gy. Then, animals from NPs and RT+NPs groups were subcutaneously injected with NPs. Tumor burden, lung metastasis and immune cell profile were explored.

Non-treated animals had progressive primary tumor growth and developed splenomegaly and lung metastases. While RT decreased primary tumor burden, Ch/γ-PGA NPs-treatment decreased systemic immunosuppression and lung metastases. The combination therapy (RT+NPs) synergistically impaired 4T1 tumor progression, which was associated with a significant primary tumor growth and splenomegaly reduction, a decrease in the percentage of splenic immunosuppressive myeloid cells and an increase in antitumoral $CD4^{+}IFN\text{-}\gamma^{+}$ population. Notably, animals from the combination therapy presented less and smaller lung metastatic foci and lower levels of the systemic pro-tumoral cytokines, and of the CCL4 chemokine, in comparison to non-treated animals. Overall, these results evidenced that Ch/γ-PGA NPs potentiate and synergize with RT, headlining their promising role as adjuvant anticancer strategies [3].

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From Positive to Negative Reflectance Response in Fibre Optics Tipped with Stacked Graphene/Dielectric Coatings

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Since its isolation [1], graphene has attracted plenty of attention as a strong candidate platform for future application in both electronic [2] and photonics devices [3]. Pristine graphene crystals can now be produced by mechanical exfoliation or chemical vapour deposition. Such methods are not appropriate for industrial manufacturing and graphene-oxide (GO) emerges as reasonable alternative [4], synthesised by simpler chemical processes. Recently, some of us [5] explored the possibility of coating an optical fibre's endface with stacked graphene/polyethylenimine films, in order to tune its internal surface reflectance.

Inspired by the previous experimental work, we present a theoretical modelling for a cleaved optical fibre with a termination coated by a stacked heterostructure of dielectric slabs separated by pristine graphene membranes (scheme in the inset of Figure 1). A study of the reflectance across an experimentally relevant spectral range is done using an optical transfer matrix method, for different parameters of the setup.

As our main result, we found an oscillatory modulation of the surface reflectance across the analysed spectral range, for number of graphene/dielectric bilayers around 10-50, with widths of a few tens of nm. Additionally, given a fixed coating, the amplitude of this modulation is shown to depend on the environment's refractive index, by either increasing (positive response) or decreasing (negative response) its surface reflectance at different wavelengths. Spectral regions of positive and negative response are separated by *"nodal points"*, where the surface reflectance is virtually insensitive to the environment. Additional studies for doped graphene membranes (simulating oxidation effects) and non-periodic (disordered) heterostructure revealed a strong robustness of these transition points to precise mesoscopic details. An example of this behaviour is depicted in Figure1.

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FIGURES

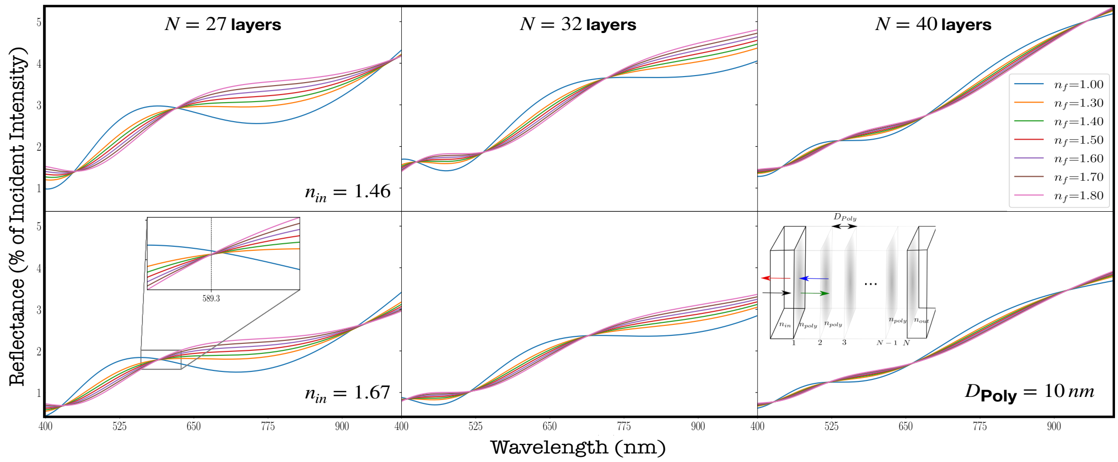

Figure 1: Surface reflectivity as a function of the incident wavelength. Termination with a coating having $N = 27, 32$ and 40 graphene/dielectric bilayers of constant width 10 nm are considered for different values of the environment's refractive index (n_f) in the range of typical fluids. The upper (lower) panels correspond to an optical fibre with an index 1.46 (1.67).

Scanning Transmission Electron Microscopy investigations of an efficiency enhanced annealed $Cu(In_{1-x}Ga_x)Se_2$ solar cell with sputtered Zn(O,S) buffer layer.

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Abstract

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) is a direct band gap semiconductor widely used in energy conversion devices due to the high sunlight absorbance and high temperature stability. A conventional CIGS solar cell is presented as a stack of glass/Mo/CIGS/CdS/i-ZnO/ZnO:Al. The highest efficiencies are typically obtained with a CdS buffer layer deposited by chemical bath deposition (CBD). However, at the industrial scale CBD generates a toxic waste since Cd is a carcinogenic material. Therefore, a transition to Cd-free buffer layers deposited by a dry vacuum process is mandatory for low-cost and environmentally friendly CIGS photovoltaic in-line production. Thus, sputtered $ZnO_{1-x}S_x$ ($ZnO_{0.75}S_{0.25}$) appears to be an alternative to the CBD CdS buffer layer in CIGS solar cells, providing a negative conduction band offset [1]. Many studies have been conducted in this direction and have shown very promising results [2]. Recently, a significant efficiency enhancement has been reported after an annealing treatment of the complete solar cell stack with the sputtered buffer $ZnO_{0.75}S_{0.25}$ [3]. This enhancement was attributed to an inter-diffusion occurring at the absorber/buffer layer interface. In this work, we investigate by advanced scanning transmission electron microscopy (STEM) techniques, the interface of a similar CIGS solar cell before and after 200°C annealing. In fact, our high resolution STEM (HR-STEM) and energy dispersive X-ray spectroscopy (EDX) demonstrate the absence of any inter-diffusion or intermixing layer at the absorber/buffer layer interface. Interestingly, we systematically observe the presence of stacking faults in close proximity to the absorber/buffer layer interface, independently from the annealing process. Finally, we demonstrate by HR-STEM imaging an order occurring between some $ZnO_{0.75}S_{0.25}$ crystals and the CIGS absorber crystals where an epitaxial relationship is observed between the $ZnO_{0.75}S_{0.25}$ and the CIGS planes subsequent to the 200°C annealing. This change at the CIGS/buffer interface could result in a lower density of interface defects, which in turn would explain the efficiency enhancement observed in the heated solar cell stack.

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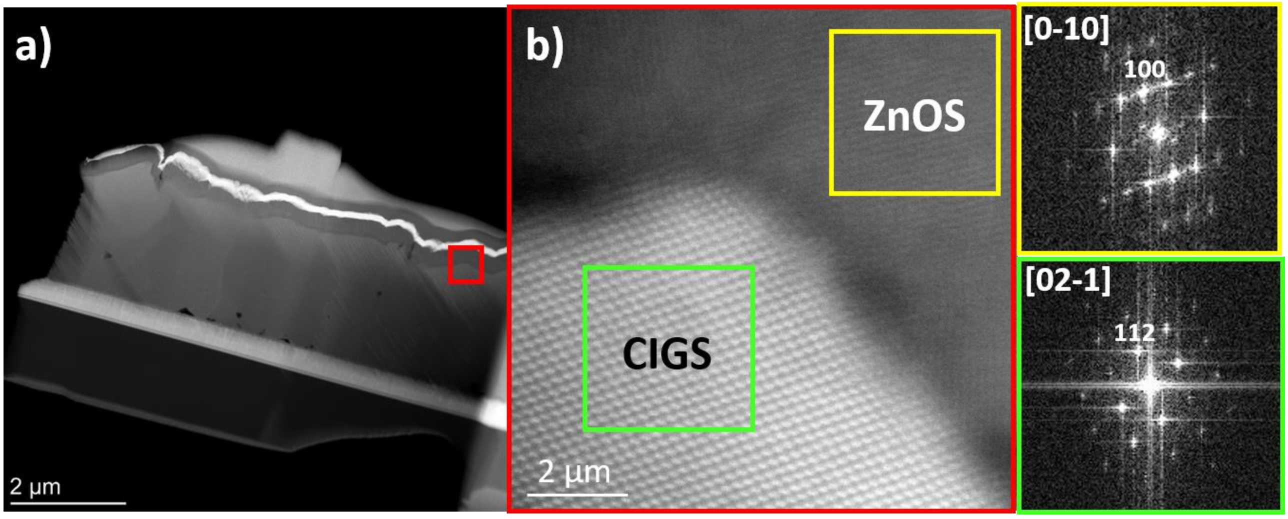

Figure 1: a) STEM-HAADF image of a FIB lamella extracted from the annealed sample. b) High resolution STEM-HAADF image of the Zn(O,S)/CIGS interface with the corresponding Fast Fourier Transform (FFT).

Synthesis, characterization and safety evaluation of gold nanoparticles

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Gold nanoparticles (AuNPs) are known to present outstanding potential for biomedical applications [1,2]. The physical-chemical properties of AuNPs, in particular their shape, seem to be critical for the biological effects of AuNPs. Gold nanostars have interesting optical properties that make them highly attractive [3]. Nevertheless, the information on their nanotoxicological properties is still very scarce. The current work aimed at synthesizing and characterizing MUA-capped star-shaped AuNPs and sphere-shaped AuNPs of similar diameter (50-60 nm), and further assessing the influence of shape on their toxicological effects. AuNPs characterization was performed using transmission electron microscopy (TEM), dynamic light scattering (DLS), UV-Vis spectrophotometry, and graphite furnace atomic absorption spectrometry (GFAAS).The toxicity, cellular uptake and permeability of the AuNPs were evaluated in vitro in non-differentiated human hepatoma HepaRG cells , primary rat hepatocytes, human epithelial colorectal adenocarcinoma Caco-2 cells and the human blood-brain barrier hCMEC/D3 cells. Viability assays as the (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) tetrazolium (MTT) reduction and neutral red (NR) incorporation assays were performed after 4 and 24 hour incubations. When toxicity was detected, other assays as the integrity of the cytoplasmic membrane by the lactate dehydrogenase (LDH) release assay and the oxygen reactive species production were included into the study. The HepaRG cells proved to be the most resistant model, while the hCMEC/D3 were the most sensitive. Overall, gold nanostars demonstrated higher toxicity and distinct cellular uptake compared to their spherical counterparts. None of the AuNPs were able to cross in vitro intestinal and/or blood brain barrier. In respect to their toxicity, these results suggest that the shape of gold nanomaterials greatly influence their interaction with the biological environment and their toxicological effect, that should be taken into consideration for biomedical applications.

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FIGURES

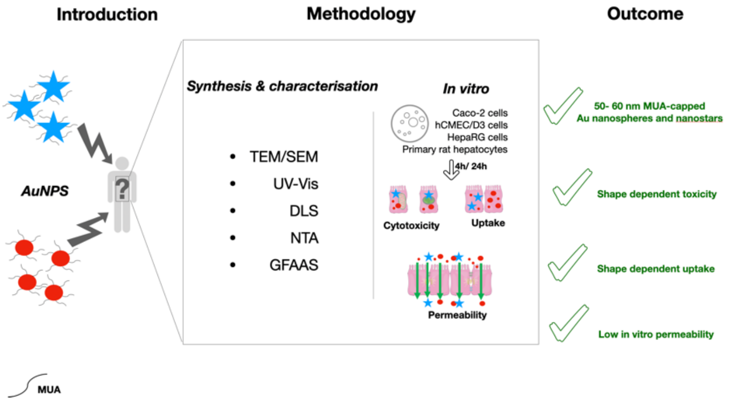

Figure 1: Graphical abstract for the shape-dependent study of AuNPs.

Electroconductive nanofiber strategies for biomaterial-based approaches to tissue engineering

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Nanofibrous scaffolds are versatile nanosystems which can be tailored into scaffolds for tissue engineering strategies. These scaffolds are perfect for the design of artificial extracellular matrices as they have high surface areas and can be easily produced through electrospinning from individual or blends of materials into single structured (monoaxial) or multilayer (coaxial) fibers. Such strategy is important do developed nanostructured materials not only to support successful cell transplantation but also to create multifunctional systems (e.g. signal to stimuli transducers, biosensors and drug delivery systems).

The role of electrical stimulation in enhancing the efficacy of cell-based therapies has been established using both *in vitro* and *in vivo models*. Electroconductive polymers are a class of materials capable of conducting electrical current, and therefore are an important component in designing multifunctional nanofibrous systems. Electroconductive coaxial fibers are an example of such system, having several advantages including tuneable mechanical properties (to boost biocompatibility), the ability to entrap sensitive drugs in the inner core layer, ease of functionalization through chemical modification and be made biodegradable.

Our group has focused on the development of electroconductive and biodegradable coaxial fibers. These systems are not only important for the development of better *in vitro* models for studying disease progression and drug testing, but also for the successful development of tissue engineering based therapies for neurological diseases. This coaxial fiber consists of a shell layer of polycaprolactone (PCL) blended with polyaniline (PANI), cladding to a core layer composed of poly(glycerol sebacate) (PGS). The development of coaxial fibers was undertaken in three sequential steps:

1. Study the effect of PANI to PCL ratio used on electrospun fibers electroconductivity vs NSC biocompatibility profile;
2. Study of the solvent system used on fiber production with electroconductivity enhancement;
3. Production of an optimal electrospun electroconductive coaxial fiber and assess its application in supporting neural differentiation of induced pluripotent stem cell (iPSC).

PCL-PANI fibers can be obtained from trifluoroethanol (TFE) solutions, with an electroconductivity plateau reached for PCL-PANI ratios 88:12, 91:9, 93:7, 94:6 and 95:5, with conductivity values in the range of 0.014 to 0.077 S cm-1. All combinations tested are biocompatible for NSC culture. However, electroconductivity was dependent on environmental humidity [1].

The solvent system for PCL-PANI fibers was optimized using TFE and hexafluoropropanol (HFP). The best combination was used to produce electrospun fibers with higher electroconductivity (0.2 S cm-1) at a higher humidity (50%). This effect was attributed both to synergic changes in PCL packaging during fiber formation and the pseudo-doping of PANI by HFP, a process that was also studied in PANI films. The AC electrical stimulation of NSCs was also performed and neural marker expression (MAP2) was improved.

Finally, coaxial PCL-PANI/PGS fibers were produced successfully. The average diameter was 951 ± 465 nm and the electroconductivity was 0.063 ± 0.029 S cm-1. The mechanical properties (ɛ of 1.3 MPa) and hydrophilicity (38 º) were also favorable for NSC culture. iPSC differentiation towards the neural lineage was favored by the presence of the coaxial fibers as shown by the upregulation of DCX, NCAM, NEUN and GAD67 neural markers.

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Fatal attraction: chitosan microspheres decorated with MSI-78A kill *Helicobacter pylori*

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Helicobacter pylori chronic infection accounts for 80% of all diagnosed gastric cancers. This gastric pathogen is one of the sixteen bacteria that ranks higher in what concerns antibiotic resistance and as a threat to human health [1]. Antimicrobial peptides (AMPs) are an interesting alternative to antibiotics due to their broad-spectrum of activity and low propensity to induce bacterial resistance. MSI-78A, an analogue of Pexiganan, is one of the few reported bactericidal AMPs against *H. pylori* [2]. However, *in vivo*, AMPs can be less effective due to proteolytic degradation and aggregation with proteins. AMPs immobilization onto a biomaterial surface is an advocated strategy to overcome these drawbacks [3].

This work intends the development of biocompatible chitosan microspheres decorated with MSI-78A (AMP-ChMic) that, after oral administration, will cross the gastric mucosa and kill *H. pylori in situ*, i.e., at the surface of epithelial gastric cells where the majority of the bacteria are found.

Chitosan (Ch) was chosen as biomaterial since it is a natural, non-toxic cationic polysaccharide, with mucoadhesive properties and has been explored in approaches against *H. pylori* [4,5]. Ch (acetylation degree of 6%) was purified and crosslinked with genipin (2.5 mM) to prevent its dissolution in gastric acidic conditions. Ch microspheres (ChMic) were produced by spray drying technique (mean diameter around 3 µm). Afterwards, a heterobifunctional spacer (NHS-PEG-MAL) was added to the ChMic that allowed immobilizing the MSI-78A modified with a terminal cysteine on the C-terminal (MSI-78A-SH) in a controlled orientation.

AMP-ChMic were successfully engineered, corroborated by Fourier Transform Infrared technique and the immobilization reaction yield was around 77%. The microspheres were able to retain their integrity in both acidic (1.2, 2.6, 4.0 & 6.0) and neutral (7.0 & 7.4) pH, proving their pH-resistance, and validating this approach for gastric settings. AMP-ChMic efficacy against *H. pylori* J99 strain, (human highly pathogenic strain) was demonstrated in a concentration dependent manner. Effect was seen as soon as 2 h and it was maintained up to 6 h, with a decrease of 3logs (from 10^7 to 10^3 CFU/mL). This result indicates that MSI-78A can retain its activity when immobilized onto ChMic.

Overall, AMP immobilization onto ChMic was successfully achieved. The selected immobilization strategy promotes AMP exposure and interaction with *H. pylori*, boosting its bactericidal performance. AMP-ChMic demonstrated high potential for *H. pylori* infection management and should be further explored within the scope of non-antibiotic therapeutic strategies.

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Production and characterization of thermoresponsive magnetic membranes

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The present work focuses on the development of multifunctional devices with Fe_3O_4 magnetic nanoparticles and PNIPAAm microgels embedded in electrospun polymeric fibers for applications in magnetic hyperthermia and drug release. Fe_3O_4 nanoparticles with an average diameter of 8 nm were synthesized by chemical precipitation technique and later stabilized with dimercaptosuccinic acid (DMSA) and oleic acid (OA) [1]. PNIPAAm microgels were synthesized by surfactant-free emulsion polymerization (SFEP) [2]. At room temperature, PNIPAAm microgels are in a swollen state a with a hydrodynamic diameter of around 1 μm and above 32 ºC, the hydrodynamic diameter decreases and at higher temperatures the collapsed state of the microgels takes place, confirming their negative temperature response and Lower Critical Solution Temperature [3]. Poly(vinyl alcohol) (PVA) was used as fiber template and a fiber diameter of 179 ± 14 nm was obtained. 10 wt. % of PNIPAAm microgels and 8 and 10 wt. % of mNPs were incorporated in the PVA nanofibers through colloidal electrospinning in order to produce composite magnetic and thermosensitive membranes. Stress tests of the composite membranes show that the incorporation of microgels and nanoparticles in the electrospun membrane increases the Young's modulus and higher concentration of nanoparticles in the membrane also leads to an increase in this parameter. DMSA coated nanoparticles appear to have a slight impact in the rise of rigidity of the membrane when compared to the OA coated nanoparticles. Magnetic hyperthermia measurements show that a higher concentration of nanoparticles and a higher amount of membrane tested leads to a higher heating ability. The composite membrane with the most promising results is the highest amount of membrane with DMSA coated mNPs, since it shows the highest temperature variation, 5.1 ºC. If we consider a body temperature of 37 ºC, a temperature variation of 5.1 ºC is enough to reach the desired 42 ºC in magnetic hyperthermia treatment making this membrane a viable option in cancer treatment. Cytotoxicity assays were performed to evaluate the cytotoxic effect of PNIPAAm microgels and mNPs incorporated in PVA membranes. All assays reveal that PVA membranes incorporated with PNIPAAm microgels and mNPs do not present any type of cytotoxicity and can be used in biomedical applications. The present work demonstrated the potential of using multifunctional composite membranes for magnetic hyperthermia and may in future be used as an alternative treatment for cancer.

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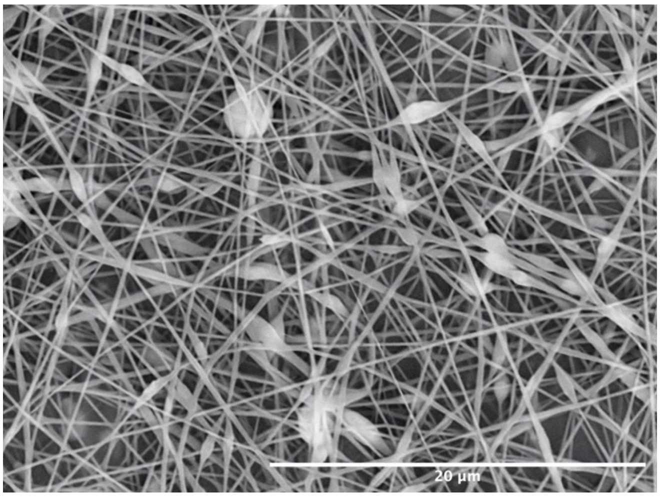

Figure 1: SEM image of PVA nanofibers incorporated with 10 wt. % PNIPAAm microgels and 8 wt.% OA coated mNPs

Green Electrospinning. From Waterborne Polymer Dispersions to Functional Nanofibers

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Electrospinning is a well-stablished technology used to create polymer nanofibers. This technology has gained extraordinary relevance in the last years due to its simplicity and low cost, as well as the possibility to effectively scale it up opening perspectives for industrial production. Electrospun nanofibers are very attractive for a broad range of applications such as textiles, filters, tissue engineering, drug delivery, wound healing, sensor, energy storage, catalysis, and many more [1–4].

Although Solution Electrospinning is the most widely used electrospinning method, it presents some limitations for industrial applications. The first limitation is the need of toxic and flammable organic solvents. The second limitation is the maximum critical concentration that can be used in this process (around 10-15 wt % of polymer). Polymer solutions of higher concentrations are not spinnable due to their high viscosity. This concentration limitation decreases the productivity of the electrospinning process importantly. Green Electrospinning is a novel and promising method that consists in the use of an aqueous polymer dispersion (latex) as electrospinning solution with the help of a polymer template. This method overcomes the above mentioned limitation as it allows the use of water as electrospinning medium, even for hydrophobic polymers, and enables to spin solutions of higher polymer concentrations increasing the overall productivity of the process [5,6].

In this work, the effect of latex properties (particle size and PSD, surface functionalization, surfactant type, solids content) that affect the final fiber morphology in green electrospinning will be analyzed. Additionally, fluorescence hybrid organic/inorganic nanofibers will be fabricated for their potential use in sensor applications.

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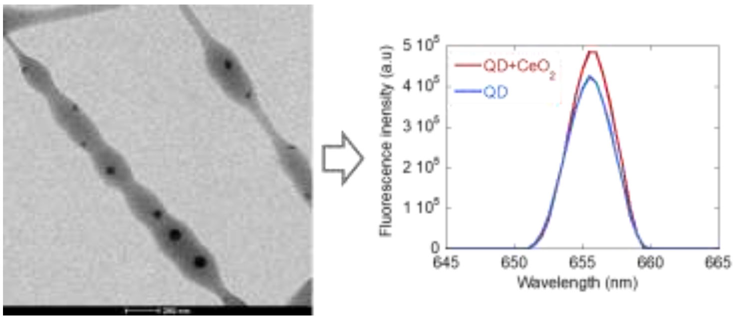

Figure 1: Fluorescent hybrid organic/inorganic nanofibers

Graphene-based films interaction with proteins, bacteria, mammalian cells, and blood constituents: the impact of surface features

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Abstract

Graphene-based materials (GBMs) availability has increased and so has the exploitation of their applications [1]. However, interaction between GBMs-integrating surfaces and the major biological systems in our body is still poorly understood [2]. The aim of this study was to systematically explore the features of these nanomaterials that most strongly impact the interactions of GBMs films with plasma proteins, bacteria, mammalian cells, and blood components [3].
GBMs films were produced by vacuum filtration using GBMs with different layer thickness and oxidation degree (graphene oxide (GO) and reduced GO (rGO) – 0.34 nm thick; few-layer graphene (FLG) and few-layer GO (FLGO) – 6-8 nm thick), which caused films to depict different surface features. After characterization by XPS, XRD, SEM, AFM, and water contact angle measurements, GO and FLGO films reveal a more oxidized (~32%), smoother (nano-roughness), and hydrophilic surface, while rGO and FLG are less or non-oxidized (13.5% and 3.5%, respectively), rougher (micro-roughness), and more hydrophobic. All films promote glutathione oxidation (Ellman's assay), indicating their potential to induce oxidative stress in biological systems: after 2 h, GO films showed the highest ability to oxidize glutathione (86.9%), followed by FLGO (50.5%) and FLG (44.0%), while rGO has reduced capacity; after 24 h, all materials reach 100% oxidation, with exception of rGO. Human plasma proteins, which mediate most of the biological interactions, were identified and quantified by mass spectrometry (nanoLC-MS/MS), adsorbing in smaller amounts to oxidized surfaces (8.3% on GO and 7.6% on FLGO) than to reduced or non-oxidized films (26.5% on rGO and 49.3% on FLG), highlighting the impact of GBMs oxidation degree on protein adsorption. Similarly, and as demonstrated quantitatively through LIVE/DEAD assay, clinically relevant bacteria – *Staphylococcus epidermidis, Staphylococcus aureus, Pseudomonas aeruginosa,* and *Escherichia coli* – adhere less to GO and FLGO films, while rGO and FLG favour bacterial adhesion and viability. Surface features caused by the oxidation degree and thickness of the GBMs powders within the films have less influence toward human foreskin fibroblasts as unravelled by Ethidium-1/Calcein/Hoechst fluorescence staining: all materials allow cell adhesion, proliferation and viability up to 14 days, despite less on rGO surfaces. Blood cells (leukocytes, erythrocytes and platelets) adhere to all films, with higher numbers in less or non-oxidized surfaces, despite none having caused hemolysis (<5%).
Unlike thickness, oxidation degree of GBMs sheets strongly impact surface morphology/topography/chemistry of the films, consequently affecting protein adsorption and thus bacteria, fibroblasts and blood cells response. Overall, this study provides useful guidelines regarding the choice of the GBMs to use in the development of surfaces depending on the envisioned application. Oxidized materials appear as the most promising for biomedical applications that require low bacterial adhesion without being cytotoxic to mammalian cells.

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Hybrid fibrous materials for advanced tissue engineering

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To mimic the natural environment of tissues, support structures are necessary in order to allow for healthy cell and tissue development. Hydrogels have become interesting materials to develop these support structures. However, hydrogels alone cannot provide all the necessary stimuli and microenvironment for cell development and, therefore, hybrid materials are currently being developed.
Cells and tissues also require more than a suitable biochemical environment [1], as electrical and mechanical stimuli are extremely important for their healthy development [2]. Scaffolds can be functionalized with nanomaterials, so these stimuli can be applied to the forming tissue [3].
Muscle is an electromechanical material, highly responsive to these stimuli [4], and the directional growth of the myoblast cells can be achieved by using aligned fibers [5].
Therefore, introducing electroactive polymers in a hydrogel scaffold, allowing for external stimulation, results in improved in-vitro mimicry of natural conditions for muscle cell growth and differentiation [6].
In this context, the present work presents the development of electrospun electroactive polymer fibers [7], to fabricate functionalized hybrid hydrogel scaffolds for muscle tissue engineering.
Oriented and non-oriented fibers, based on electroactive, biocompatible, biodegradable and biostable polymers, have been processed and characterized. They were further modified with ionic liquids and magnetic particles to allow electro and mechanotransduction to be applied to the cells.
This resulted in fibers with diameters between 0.5-3 µm, crystallinity between 45-60%, electroactive phase content around 90%, with the thermal stability of the polymer being unaffected by the inclusion of these materials. The results confirm the suitability of the materials for biomedical applications.

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Crystallization and Glass Transition of Polymers Interacting with the Square-Well Potential

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Crystallization in general atomic and particulate systems is of paramount importance in the development of novel materials with enhanced characteristics. Its understanding, especially at the molecular level, is thus critical to connect atomic structure with the macroscopic behaviour of the end material. Despite of its relevance and the ever-growing body of published literature, there are still numerous unsolved questions around the crystallization of complex macromolecular systems, especially since chain crystals are formed under special processing conditions and confer unique properties to the corresponding systems. In the present work, we employ Monte Carlo simulations to study the phase behaviour of linear, freely jointed chains whose spherical monomers interact through the pair-wise Square Well (SW) potential [1]. Compared to the typical, excluded-volume, Hard Sphere (HS) model, the SW potential allows the systematic study of how intensity and range of interactions affect the phase behaviour. A wide variety of different structures are obtained by varying the model parameters: from amorphous clusters to well-ordered ones, consisting of virtually perfect FCC, HCP, HEX and BCC crystals. When critical values of both interaction parameters are met, clusters form fivefold-rich local structures leading effectively to vitrification. We further study the cluster formation under dilute conditions and the short- and long-range structure of polymer chains. Present results allow the systematic comparison between the energy-driven crystallization in SW systems and entropy-driven crystal nucleation of athermal polymers [2] and the behaviour of chemically more complex macromolecules [3]. Such insights can help the design of novel colloidal and granular polymers with short-range attraction.

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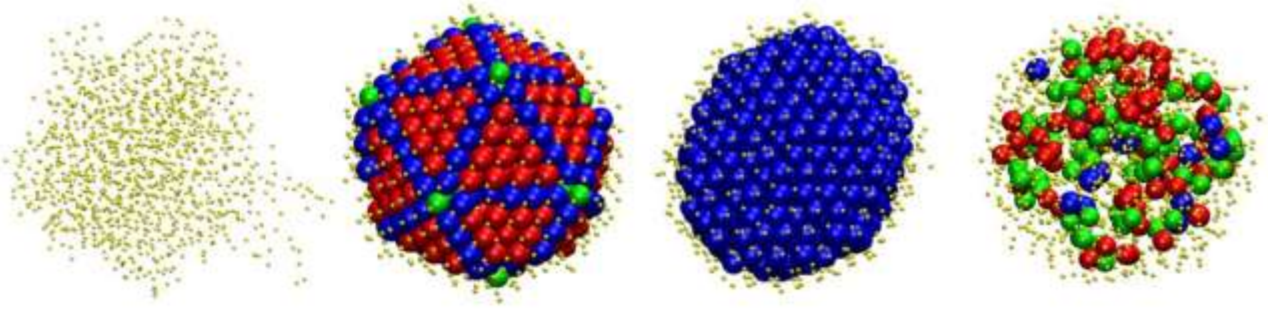

Phase behavior of clusters of chains interacting with the square well potential

Figure 1: Snapshots of several system configurations at the end of the simulations. Monomers are color-coded according to its similarity to given crystal structures.

All in one: Laboratory-on-a crystal for multifunctional, multiscale probing of thin films

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We developed a novel experimental platform to correlate optical, electrical, gravimetric, and viscoelastic properties of thin films under controlled environment. This new platform enables high-throughput multifunctional materials characterization on a continuous scale, from meso scale down to nanoscale on the same sample. The system uses specially modified AT cut quartz crystal microbalance, QCM, to enable electrical (impedance, resistance), optical, gravimetric, viscoelastic measurements simultaneously under controlled environment (light, gas, vapor atmosphere). Specially designed 3D printable cell can be printed using materials suitable for aggressive environment while conducting multimodal testing. We demonstrated seamless operation of platform and characterized same area of thin film composite using confocal fluorescence imaging (sub-micron resolution) and using multimode AFM (nanoscale) thus creating a continuous (macro-to nano) scale map of the composite dynamic functionalities. Changes in the frequency dependent QCM for different environmental conditions and scanning probe microscopy (SPM) were used to tease out the correlation between macroscale changes in shear modulus and viscosity and local elastic modulus of composite film. We will show how machine learning tools can be used to correlate different functional properties of a thin film during exposure to environment during exposure to environment. The Laboratory-on-a-crystal is now part of CNMS user capabilities.

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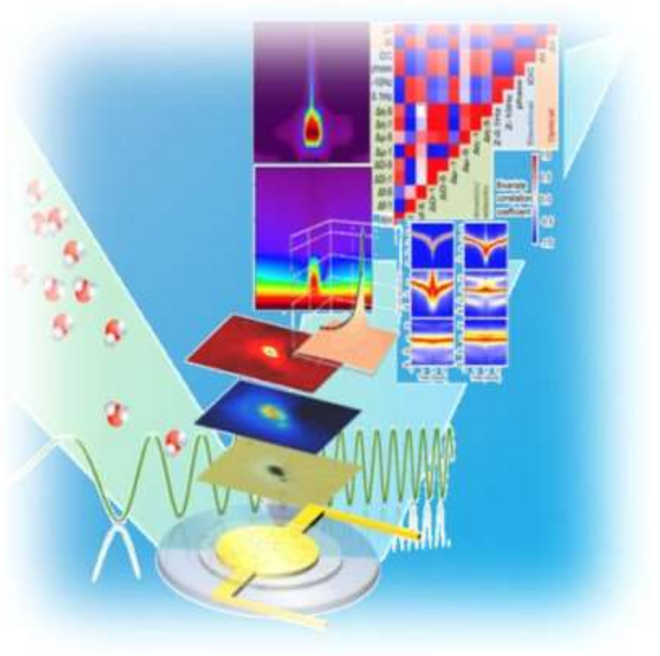

Nonperturbative momentum dependency in diagrammatic calculations

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The study of disorder in Condensed Matter Physics is as old as the field itself. Disorder can supress desirable material properties such as the conductivity but it can play a fundamental role in quantum phase transitions and can even be shown to enhance superconductivity [1]. The requirement of a realistic quantum description of disorder led to the development of diagrammatic techniques which are able to deal with disorder in a controlled way [2,3] by expanding the disorder averaged Green's function in powers of the disorder strength or the impurity concentration. Several approximation schemes may be employed in order to resum an infinite subseries of diagrams, such as the self-consistent T-matrix approximation and the Born approximation. While nonperturbative, these approaches typically fail to capture any momentum dependency of the Green's function not coming from the dispersion relation. Here, we present a nonperturbative method to capture the momentum dependency of the disorder in the disorder-averaged Green's function, effectively summing a larger subset of diagrams. We use KITE [4,5] to apply this method to several 2D systems such as the square lattice subject to Anderson disorder, graphene with vacancies and $SrRuO_3$.

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FIGURES

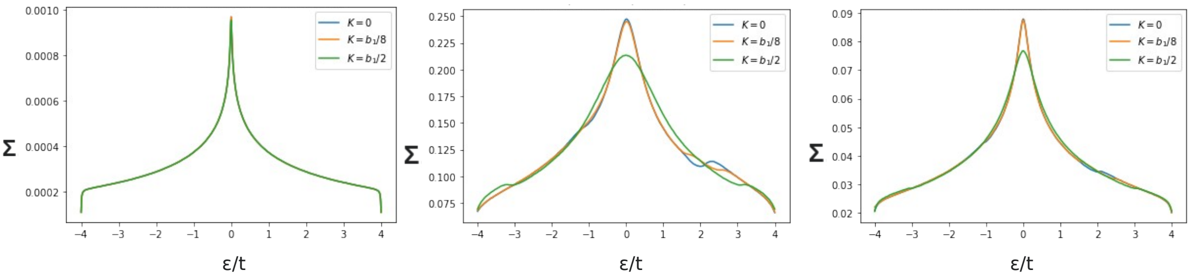

Figure 1: Self-energy of the square lattice as a function of energy for several values of the electron momentum and Anderson disorder strength. Diagrammatically, momentum-dependent diagrams should become relevant for higher values of the disorder strength, as is seen here.

Post-Deposition Treatment and Rear Interface Passivation in ultrathin Cu(In,Ga)Se$_2$ solar cells

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Currently, Cu(In,Ga)Se$_2$ (CIGS) solar cell researchers are focusing their attention on reducing the absorber thickness from the standard 2 µm to the ultrathin range (i.e. around 500 nm). However, ultrathin CIGS devices have their electrical performance limited by electronic losses, mainly caused by rear interface recombination [1]. In order to tackle such losses, one strategy is the use of a dielectric layer to passivate the rear interface [2]. However, there are a few reports where the performance of ultrathin passivated devices is lower when compared with reference non-passivated devices. In this work, to better understand the passivation effect in ultrathin CIGS devices, a point contact nanofabricated structure based on an Al_2O_3 dielectric layer was employed together with a post-deposition treatment (PDT) by potassium fluoride (KF). E-beam lithography was used to pattern the Al_2O_3 layer to establish an electrical contact at the rear interface. The fabricated devices solar cell structure is shown in Figure 1. Current density vs Voltage (J-V) measurements show that when passivation is present without KF-PDT (PassAl$_2$O$_3$) then open-circuit voltage (V_{OC}) values achieve 426 mV, which is 93 mV lower than devices with only KF-PDT (PassKF), 519 mV. The application of both treatments (DoublePass) leads to an increase in V_{OC} values of 176 mV over PassAl$_2$O$_3$ (602 vs 426 mV, respectively) and 85 mV over PassKF (602 mV vs 519 mV, respectively). Temperature vs V_{OC} measurements indicate that interface recombination is the predominant recombination mechanism in devices with only one passivation strategy(PassKF and PassAl$_2$O$_3$). The application of both treatments in the DoublePass device lead to an interfaces passivation, with bulk recombination being the major recombination loss. These results may indicate that rear passivation is only effective when rear interface recombination is the dominant loss factor. Time Resolve Photoluminescence, Capacitance vs Voltage, admittance circuit fitting measurements and SCAPS 1-Dimensional solar cell device simulations are presented to support the observed experimental results.

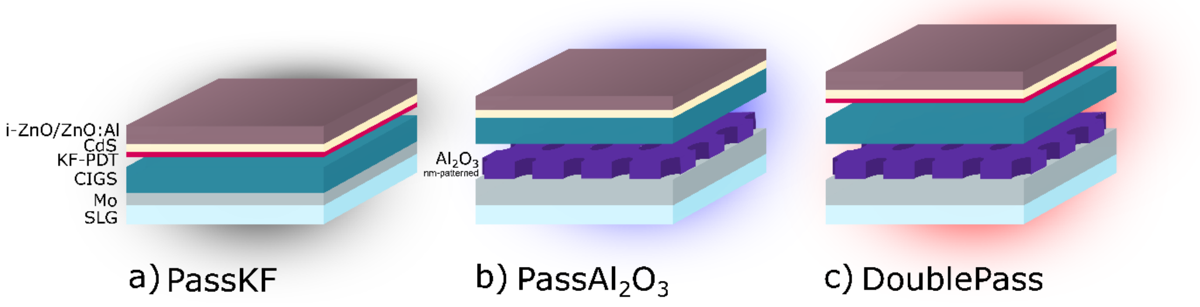

Figure 1: Schematic of the fabricated devices: a) device with only PDT, PassKF; b) device with only rear interface passivation layer, PassAl$_2$O$_3$; c) device with both treatments, KF-PDT and rear interface passivation, DoublePass.

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Composites of biopolymers and metal oxide nanoparticles for controlled release of micronutrients in agricultural soils

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Zinc micronutrient deficiency is a common problem in soils worldwide. Zinc is crucial for plant growth and development as it takes part in a range of plant biochemical processes. Zn is vital for the regulation of plant growth hormones, the maintenance of healthy root systems and the preservation of tolerance to plant stressors [1,2]. To correct Zn deficiency and prevent crops losses, fertilizers containing Zn are added to the soils. Due to lack of synchronization between the release of Zn from conventional ionic fertilizers (Zn as salt or chelated forms) and the uptake by plants, along with the high mobility of ionic species in soils, only a small part (30-50%) of the fertilizers applied to the soils are actually used by plants [2]. The remaining Zn applied forms nonbioavailable complexes in soils, or it is removed by leaching or runoff, causing negative environmental impacts [2]. Zn-based engineered nanomaterials (ENMs) can be used to control the release of Zn in soil/plant systems according to specific soil biochemical conditions, plant species, and plant life cycle stages, allowing a reduction of nutrient loss and of fertilizer application rates [3]. In the present work [4], composites of biopolymers (microcrystalline cellulose, chitosan, and alginate) and ZnO nanoparticles (NPs) were prepared and characterized. The potential of these materials for the controlled release of Zn, in acidic agricultural soils, was tested and their impact on the growth of maize plant was assessed. Comparative studies using $ZnCl_2$ and ZnO NPs not immobilized in the biopolymer were also performed. While $ZnCl_2$ salt leached from the soil resulting in very low extractable Zn concentration, Zn in ZnO NPs was less labile, and ZnO NPs/alginate beads maintained a better constant supply of extractable Zn than all other treatments, at least over the 30 days of experiments. Results further indicated that ZnO NPs/ alginate beads could meet the maize Zn needs while avoiding the early stage Zn toxicity induced by conventional ionic Zn supplies. Perspectives of applications and required environmental impact assessment will be discussed, namely by considering that these ENMs might be a sustainable way to supply Zn in a controlled manner in acidic soils.

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Biodegradable pHEMA containing graphene oxide for blood contacting applications

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Abstract

Blood contacting devices are widely used for the treatment of cardiovascular diseases. Small diameter vascular grafts (SDVG) (Ø<5mm) are often required, for instance in coronary or peripheral artery disease, as a strategy to reestablish the blood flow. However, the lack of a biomaterial to successfully replace the native small diameter vessels, avoiding infection and thrombus formation, demands improvements in this field [1, 2]. Our group has recently demonstrated that poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogels may be produced with high-strength and stiffness by combining it with graphene oxide (GO) [3], enabling its use as an inert SDVG.

The present work aims to develop a post-implantation tissue engineering approach for SDVG applications. For that, a new degradable biomaterial was designed by developing a degradable pHEMA (d-pHEMA) in combination with GO to achieve improved mechanical properties.

d-pHEMA films were produced by adding a degradable cross-linker pentaerythritol tetrakis(3-mercaptopropionate) (0.25-0.75wt.%), named as tetrakis, to a previously described formulation with and without a non-degradable cross-linker (tetraethylene glycol dimethacrylate, TEGDMA) [4]. Polymerization of all formulations was confirmed by FTIR, where no evidence of unreacted HEMA monomers (C=C; 1635 cm^{-1}) were observed. Similarly, water uptake and optical contact angle have demonstrated that tetrakis presence does not induce significant changes on swelling and hydrophilicity (~40°) of the native pHEMA, maintaining pHEMA hydrogel-like and non-fouling behaviors. This was also confirmed *in vitro* in a cell adhesion assay, where no human umbilical vein endothelial cells (HUVECs) adhered to d-pHEMA nor d-pHEMA/GO materials surface, after 1 and 7 days.

In vitro degradation studies showed that d-pHEMA with 0.75% Tetrakis (0.75T) totally disappear after 6 months, contrarily to other formulations. This was also verified *in vivo* in chorioallantoic membrane (CAM) assays, where 0.75T samples disappeared. Upon GO incorporation, the stability of the samples increased. The 24h degradation products were assessed using HUVECs, where no cytotoxicity was observed. These results are promising regarding a future application in SDVG, once d-pHEMA is cytocompatible with HUEVCs.

Mechanically, it was shown that incorporation of tetrakis decreased the young modulus and tensile strength (UTS). However, upon 1%GO addition, UTS increased to 0.06 MPa while keeping a strain of 39% (0.25T samples).

The new developed composite hydrogel d-pHEMA/GO has demonstrated to be biodegradable while keeping the essential properties for SDVG production.

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Supramolecular Two-Dimensional Peptidic Adhesives for Graphene Oxide Fiber Functionalization

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Amino-terminated oligoglycines non-covalently self-assemble, through cooperative hydrogen bonding formation, into biocompatible rigid 2D nanostructures called tectomers. Tectomers effectively coat carboxylated multi-walled carbon nanotubes (MWCNT-COOH) and strongly interact with graphene oxide (GO). Electrostatic interactions and hydrogen bonding formation accounts for the strong interfacial interaction of tectomers with MWCNT-COOH and GO, respectively [1].

Because of the high affinity of tectomers to GO, tectomers have been used to coat wet-spun GO fibers [2]. We here show that, due to their versatile surface chemistry, tectomers act as supramolecular adhesives for nanomaterial and molecule immobilization on the GO fiber surface. Tectomer-coated GO fibers can then be subsequently decorated with a variety of carbon nanomaterials (carbon nanotubes, carbon nanohorns, carbon nanocones, and highly fluorescent nanodiamonds), metal (gold, platinum, iron) nanoparticles, acrylate-based polymer nanoparticles, fluorophores and drugs. The resulting ultrathin coatings exhibit remarkable water resistant properties. We show that this tectomer-based "double-sided sticky tape" fiber functionalization strategy can be extended to other fibers and fabrics, such as polyurethane/PEDOT:PSS, poly(methyl methacrylate) and polyester, making it very attractive for a variety of technological and smart textile applications [3].

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Novel rear structure design for an effective optical enhancement in ultrathin $Cu(In,Ga)Se_2$ solar cells

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Amongst all the thin film solar cells technologies, $Cu(In,Ga)Se_2$ solar cells stand out, due to presenting the foremost power conversion efficiency value (23.35 %), and for satisfying the requirement for new application possibilities imposed by the photovoltaic industry [1]. Nonetheless, sub-μm ultrathin solar cell absorbers have been gaining relevance, as they allow to meet economic and technological targets through cost-reduction objectives [2]. However, the thickness reduction comes with drawbacks, such as, a decreased light absorption and increased interface recombination. To tackle the imposed downsides, light management as well as interfacial passivation strategies need to be employed. In this work, a novel light management architecture is used to enhance the optical path in the absorber. Gold nanoparticles (NPs) aggregates were integrated at the solar cell rear contact and encapsulated with a dielectric matrix commonly used as a passivation layer in solar cells. The rear substrate fabrication procedure is represented in **Figure 1**. This way, an encapsulation strategy shielding the fabricated nanostructures from the high temperatures and harsh processing conditions of the remaining device is coupled with a passivation approach to reduce rear interface recombination. An X-ray photoelectron spectroscopy analysis was conducted demonstrating the effective encapsulation of the Au nanostructures. With the novel rear architecture, a broadband external quantum efficiency increase was obtained, leading to a 17.4 % increase of the short circuit current density value over a reference device.

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FIGURES

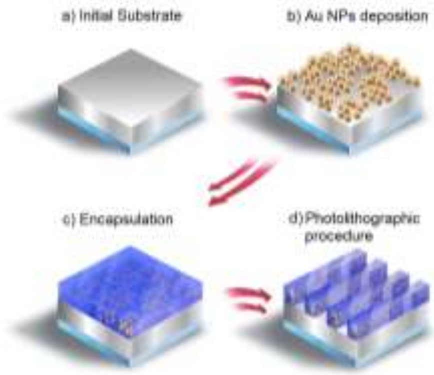

Figure 1: Schematic illustration rear structure fabrication. a) Initial substrate. b) Au NPs deposition. c) Au NPs encapsulation with a 25 nm Al_2O_3 layer. d) Photolithographic procedure allowing for an electrical contact. Taken from [3].

Sticky cellulose hydrogel as reusable a platform for a SERS based immunoassay

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Abstract

Immunoassays using Surface-Enhanced Raman Spectroscopy (SERS) are especially interesting on account not only of their increased sensitivity, but also of their easy translation to point-of-need formats. The basis for these assays are bioconjugates of polyclonal antibodies and anisotropic gold nanoparticles functionalised with a Raman reporter. These bioconjugates, once loaded with the antigen analyte, can react in a sandwich format with the same antibodies linked to a surface that is used for detection on a microfluidics or immunochromatographic platform. The detection success depends upon the binding event, thus an appropriate immobilisation of antibodies necessary for subsequent reaction on the selected surface is mandatory. Here, we used bioconjugates of gold nanostars functionalised with 4-mercaptobenzoic acid, and anti-horseradish peroxidase antibodies and a sticky cellulose-based membrane. All steps of bioconjugate formation were fully characterised by Ultraviolet-Visible Spectroscopy, Dynamic Light Scattering, Scanning Electron Microscopy and Agarose Gel Electrophoresis [1]. The bioconjugates, together with the sticky cellulose-based membrane functionalised with anti-horseradish peroxidase antibodies, were used for SERS applications, resulting in an immunoassay with demonstrated functionality for antigen detection. The sandwich immunoassay platform proved to be able to detect the immunocomplex formed and perform a multiplex assay through direct classical least squares method application [2]. The cellulose-based membrane allowed a good uniformity of SERS signal, and a good reproducibility when different functionalisation batches were tested (Relative Standard Deviation of 13%). Furthermore, these SERS platforms remained stable after 168h of storage and presented a regeneration capability of seven cycles. Since the antibody used was a generic IgG antibody, the subjacent principle of this platform can be applied to screen detection assays of other antibody-antigen systems.

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Graphene: The key for pHEMA application as blood contacting devices

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Thrombosis and infection are the leading failure causes of blood-contacting devices (BDC), mainly due to poor performance of existing biomaterials[1]. Poly(2-hydroxyethyl methacrylate) (pHEMA) has excellent hemocompatibility, but the weak mechanical properties impair its use as bulk material, being solely explored as a coating. However, instability and difficulty of attachment to the underlying polymer compromise the coating success. This work unravels the use of nanomaterials, namely graphene-based materials (GBM), to reinforce pHEMA, creating composite hydrogels that meet the biological and mechanical requirements to stand-alone as BCD.

GBMs with different exfoliation, oxidation degree and lateral size were used, namely graphene nanoplatelets (GNP M5 and M15), oxidized GNP (GNP M5ox and M15ox) and graphene oxide (GO). GBM were either purchased or produced by modified Hummers' method and characterized by TEM and XPS. pHEMA/GBM composites were produced by *in situ* polymerization of 2-hydroxyethyl methacrylate and tetraethylene glycol dimethacrylate in the presence of the different GBM[1]. Resulting composites were evaluated regarding GBM dispersion and surface topography (SEM), wettability (contact angle), swelling capacity (gravimetry) and mechanical properties (tensile tests). Biocompatibility of pHEMA/GBM was evaluated by assessing the medium extracts cytotoxicity towards HUVECs cells. Non-fouling properties of pHEMA/GBMs were evaluated by assessing their capacity to adhere human platelets (SEM), HUVECs cells (fluorescence microscopy) and bacteria (high-throughput microscopy). A prototype conduit of pHEMA/GO (ID: 4 mm; OD: 6mm) was developed to evaluate its blood compatibility *in vivo* using non-heparinized pigs as animal model. Conduits were connected to pig carotid arteries (A-V shunt), being in contact with circulating blood for 30 min, and materials surface lumen evaluated by SEM.

The lateral size of GBMs ranges from 1.5 to 15 µm, being GO the smallest material. Oxidized forms of GBMs show similar oxidation degree (34%O) and non-oxidized GBMs have low oxygen content (3%O). GO has the highest exfoliation degree. Incorporation of GBMs in pHEMA increases its surface roughness but keeps its surface wettability (contact angle of 25º) and swelling capacity (50%). Among the tested GBMs, GO was the most efficient filler, increasing pHEMA's stiffness and tensile resistance, reaching 2 MPa and 0.7 MPa, respectively. These values empower the application of pHEMA/GO composites in development of blood contacting devices, including small diameter vascular grafts.

Regarding the biological properties, pHEMA/GBMs extracts are not cytotoxic and pHEMA/oxidized GBMs maintain the non-fouling properties of pHEMA, exhibiting negligible levels of adherent cells, blood platelets and bacteria. In vivo hemocompatibility studies show that pHEMA/GO conduits withstand the blood pressure and exhibit negligible adhesion of blood components, revealing better hemocompatibility than ePTFE, a commercial material for vascular assessment.

Our findings reveal pHEMA/GO, a synthetic and off the shelf hydrogel, as a preeminent material for the design of blood-contacting devices that prevent thrombosis and bacterial adhesion.

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Portable graphene transistor sensing system for wine DNA detection

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Miniaturized sensing system has been a spotlight in various detection schemes for a wide application owing to its portability, low-cost and rapid response. Especially in pandemic scenes, most of the attention from both government, researchers, and societies are focused on the rapid medical diagnosis. Little is addressed to the slow rippling effects of the outbreak on the food sector, such as in the limited food supply chain [1]. Besides the threat of food supply shortage, the risk of food fraud is potentially increased due to disrupted food material distribution. Therefore, less laborious and rapid food analysis protocol is urgently required to speed up not only the typically time-consuming “farm-to-fork” analytical process” [2] but also to control the good business practice for the food safety and security. In this study, a single layer graphene-based field-effect transistor (FET) chip integrated into a compact readout system is used to identify a unique DNA sequence from the wine of Douro protected Designation of Origin (PDO), one of the most important products in Portugal. Graphene has been highly noted for its paramount characteristics for ultrasensitive biomolecular detection due to its two dimensional (2D) with only 1-atom thick carbon structure [3]. The biorecognition process on the graphene FET channel in this work was performed through surface functionalization with a pyrene-based linker via π- π stacking interaction [4]. The process was followed by single-stranded DNA immobilization onto the interface and ethanolamine blocking of the unreactive sites of the linker. The introduction of the complementary single-stranded DNA allowed the hybridization to occur, leading to the shifting of the Dirac point (V_{Dirac}) of the graphene [5]. The chip with multi-arrayed sensors was integrated with a mini-output reader packed in a “business-card” size, practically linked and controlled from a computer. Before the detection of DNA, surface functionalization stages were tested with the integrated sensor and validated with Raman analysis. In the DNA hybridization study, the proposed system was able to perform a distinction of full complementary DNA and single nucleotide polymorphism (SNP) type DNA with a single mismatch, as shown by about 14% sensitivity difference tested from a considerably wide dynamic range. The overall results denote the potency of the proposed device for the wine authenticity checking in a rapid and portable fashion as well as multiplex detection by the multi-arrayed sensor configuration.

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FIGURES

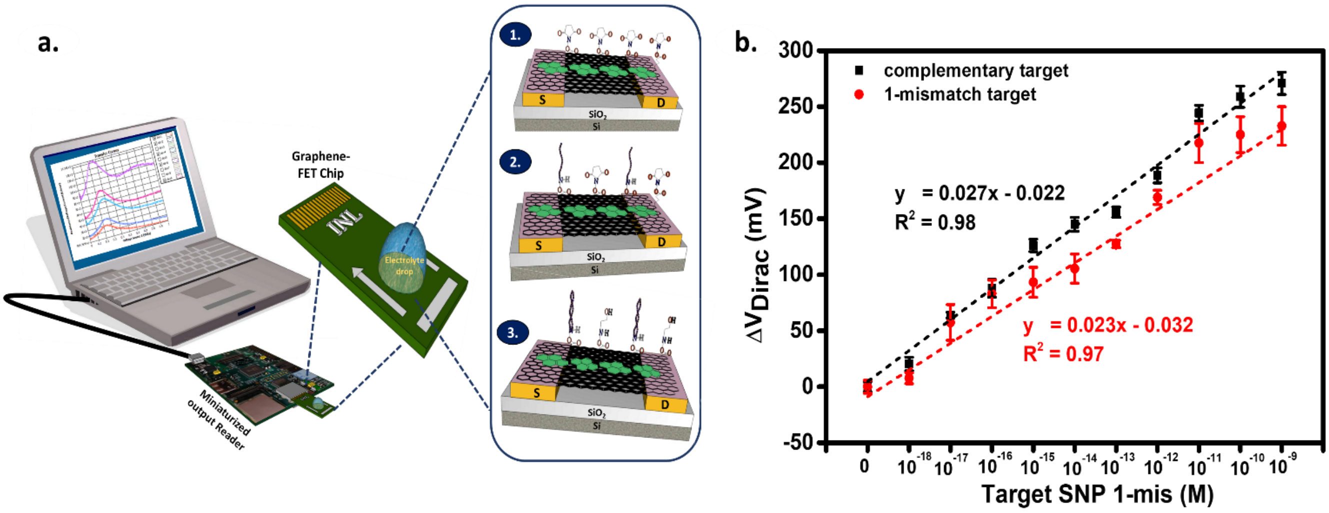

Figure 1: a. The proposed setup of the portable graphene FET sensor and surface functionalization for DNA hybridization study, b. The calibration plots from the measurement of wine DNA hybridization using complementary and single-mismatch DNA target.

Modification of a transparent binder for road pavements using TiO_2 nanoparticles

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Light and heat are relevant factors for road pavements since they promote the aging of the asphalt surfaces [1], and a large amount of heating can intensify the Urban Heat Island (UHI) effect [2]. Contrariwise, the lack of light strongly affects visibility conditions, reducing safety [3]. The conventional black color of asphalt pavements absorbs light and stores a large amount of thermal energy, which can be reduced opting by the application of light-colored pavements using, for example, a transparent binder [3]. Industrial activities and road traffic are the main sources of pollutant emissions, mostly SO_2 and NO_x, which are hazardous atmospheric pollutants. There are several consequences at different scales caused by these harmful gases, such as intensification of the greenhouse effect, acid rain, and public health problems. With the use of nano-TiO_2 into/over asphalt mixtures, and consequently with the functionalization process considering the photocatalytic and self-cleaning properties, road pavements become the ideal places to mitigate environmental pollution due to proximity to the emissions [4]. If a transparent binder modified with nanoparticles of TiO_2 is used, pavements will present multifunction effects and benefits when submitted to high solar irradiation. The production at laboratory-scale of such pavements is presented in Figure 1. First, the transparent binder was modified with nano-TiO_2 (0, 0.5%, 3.0%, 6.0% and 10.0%). Binder's workability was confirmed. It presented similar behavior as a polymer modified binder. In these binder samples, the addition of high contents of nano-TiO_2 increased the rutting resistance, but it seemed to reduce fatigue life, except for the 0.5%. Also, the nano-TiO_2 modification had a slight effect on the chemical functional indices. The best percentage of TiO_2 was 10.0% considering rutting resistance and 0.5% concerning fatigue life.

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FIGURES


a) b) c) d)

Figure 1: a) Binder Modification with nano-TiO_2; b) asphalt mixture production; c) asphalt mixture compaction; d) slab sample of a light-colored pavement.

Direct characterization of functional materials by haptenized fluorescent dendrimers for in vitro allergic drug diagnose.

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β-lactams are the most widely drug prescribed against infections, but they are the most commonly reported medication allergy too. A correct diagnosis of these allergic reactions is crucial to avoid rejecting them by other more expensive broad-spectrum antibiotics, with potential risk factors for the development of multiple drug-resistant bacteria. [1] Skin testing is the most consensual approach to diagnose β-lactam allergy, but this *in vivo* test is not risky free and should be performed under strict hospital surveillance.[2] *In vitro* testing is not still widely used on account of their low sensitivity. We report the use of already haptenized fluorescent dendrimers [3] to control the preparation of materials for *in vitro* test, and their verification by testing on patient sera samples. This fluorescent dendrimer is obtained from a dye with two orthogonal functional groups suitable for click chemistry. [4]

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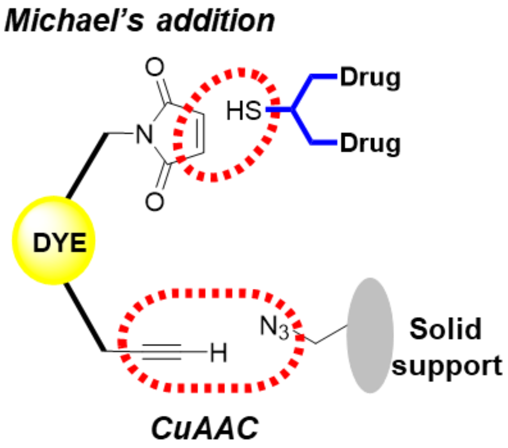

Figure 1: Toward the synthesis of a fluorescent macromolecular carrier from a model with two orthogonal functional groups able to react through two different click chemistry reactions.

$Cu(In,Ga)Se_2$ growth by magnetron sputtering with Cu-rich and Cu-poor targets

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High-efficiency $Cu(In,Ga)Se_2$ (CIGSe) thin-film solar cells are typically fabricated by a multi-stage co-evaporation process, where one of these stages leads to a Cu-rich composition [1]. Cu-rich conditions favor the growth of CIGS grains, improving the overall efficiency of the solar cell [2]. In this work, we explore the effect of the copper stoichiometry of sputtering targets on the grain size of the CIGSe absorber and on the efficiency of the solar cells. $Cu(In,Ga)Se_2$ absorber layers were deposited on Mo/soda-lime glass substrates under the same conditions with two different Cu-In-Ga targets: $Cu_{0.6}In_{0.25}Ga_{0.15}$ and $Cu_{0.5}In_{0.35}Ga_{0.15}$. Selenium was supplied simultaneously by a pulsed valved-cracker evaporation source [3]. Scanning electron microscopy analysis revealed that CIGS films sputtered with the Cu-rich target exhibited larger grains than those deposited with the Cu-poor target (Fig. 1). To fabricate complete solar cells, the CIGSe layers were submitted to a KCN-etching process to remove $Cu_{2-x}Se$ impurity phases, after which a CdS buffer layer was deposited by chemical bath deposition and a i-ZnO/ZnO:Al double layer was sputter-deposited as the front contact. Solar cells based on the Cu-rich deposited CIGSe absorbers show better photovoltaic parameters compared to those based on the Cu-poor deposited CIGSe, as evidenced by current-voltage curves (Fig. 2). We attribute the improved performance to the larger grain size enabled by the Cu-rich growth conditions.

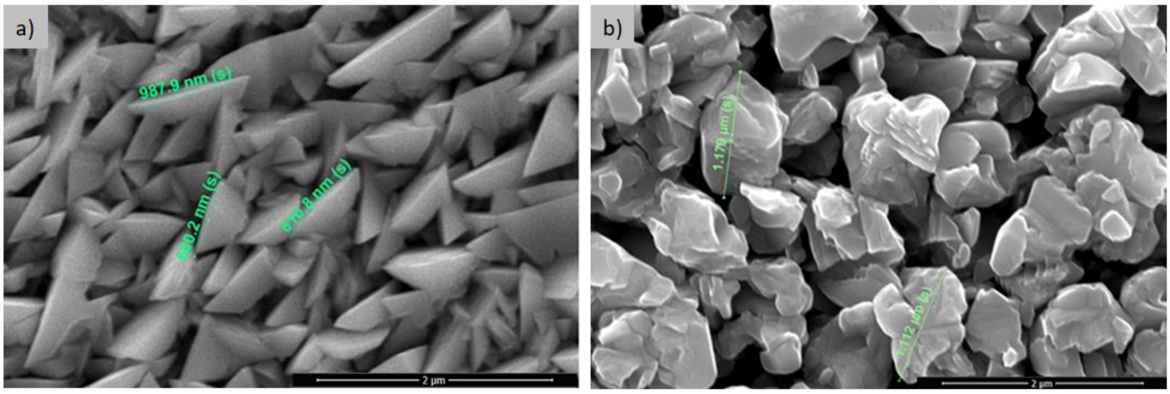

Figure 1. CIGS crystals grown at 400°C with (a) Cu-poor target and (b) Cu-rich target.

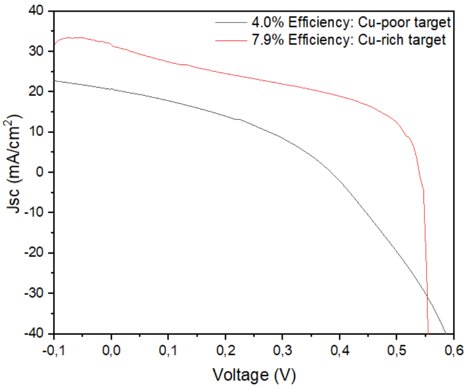

Figure 2. I-V curve of the best solar cells achieved at a deposition temperature of 400ºC with Cu-poor and Cu-rich targets.

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Graphene transistors for biosensing: optimizing the microfabrication process

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Electrolyte-gated graphene field-effect transistors (EG-GFETs) have been explored for biosensing applications with promising results [1] for a variety of biomolecules such as, proteins, nucleic acids and hormones [1]. However, most of the results never go over the proof-of-concept stage mainly due to reproducibility and scalability issues. The main goal of this work is to develop a process for wafer-scale fabrication of high electronic quality graphene devices for biosensing applications. Our process overcomes two main issues: dielectric passivation of metallic contacts and removal of surface residues after graphene transfer and patterning.

Dielectric passivation of metallic contacts was optimized considering the need to use strong solvents (e.g., DMF) when functionalizing graphene [2] and recurrent exposure to saline solutions. A protective coating consisting of a stack of five alternated SiO_2 and SiN_x thin-film layers with a total thickness of 250 nm was designed. To achieve full protection of the passive areas of the chip with sub-device resolution (the active channel area for biosensing is defined at this stage), the protective layer is applied after graphene transfer and subsequently dry-etched. This requires the use of a protective layer for the graphene itself, to allow patterning of the dielectrics by RIE.

CVD graphene is normally transferred to the final substrate using a temporary polymeric substrate. Although it is the best method for large-scale transfer, it brings about challenges due to surface contaminants (PMMA, metal residues) [3], often overlooked in the biosensing field, which hinder functionalization and promote non-specific binding of biomolecules in undesired areas [4]. To avoid the adherence of transfer-borne residues to the EG-GFETs critical surfaces (e.g., in-plane gold gate electrode) graphene transfer assisted by lift-off methods was successfully explored in layouts with low device density. For denser designs, however, a protective metallic layer was added on top of the gold contacts leaving only the graphene-receiving areas exposed. The protective layer endures multiple wet-transfer and full-wafer processes and survives all steps required for graphene patterning. In the end, the protective layer is easily removed by mild chemicals, providing a fast and safe way to avoid residues on the final surface of the devices.

Electrical characterization of the devices shows good coverage of graphene and process uniformity. A statistical study of the channel resistances showed that the value of the channel resistance depends critically on the quality of the graphene transfer step.

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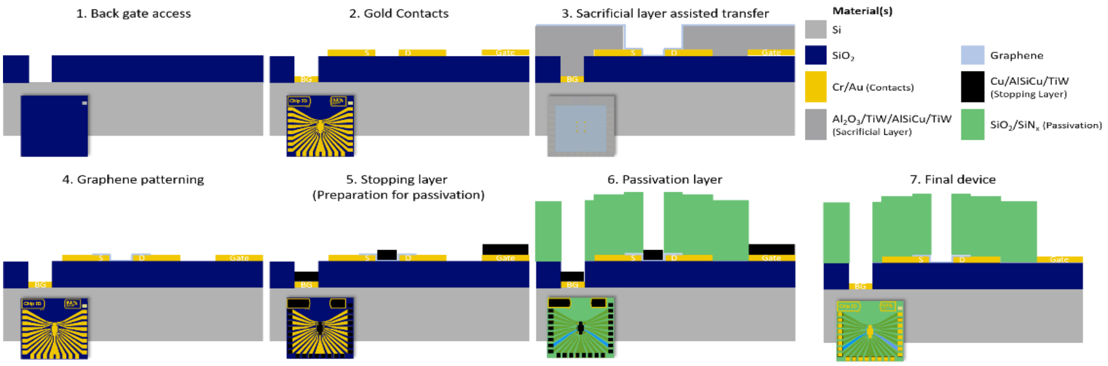

Figure 1: Graphical overview of the optimized fabrication process for wafer-scale production of EG-GFETs for biosensing.

Magnetic Nanosorbents Prepared from Quaternary Chitosan for the Removal of Glyphosate from Water

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Glyphosate (GLY) is a non-selective and broad-spectrum type of organophosphorous herbicide used worldwide. Water resources contamination with GLY is a threat to public health and ecological systems [1]. Thus, there is an urgent need for efficient procedures capable of purifying contaminated water and meeting quality standards. Here we describe magnetic bio-hybrids prepared from trimethyl chitosan (TMC), which is a quaternary chitosan scarcely studied for environmental applications. Core@shell composite colloidal particles comprising a core of magnetite (Fe_3O_4, ~50 nm) uniformly coated with TMC-siliceous hybrid shells (Fe_3O_4@SiO_2/SiTMC) were successfully prepared using a one-step sol-gel coating procedure [2]. Adsorption experiments were conducted to investigate the potential of the coated particles for the magnetically assisted removal of GLY from ultra-pure water and wastewater samples. For the synthetic water samples, the magnetic nanosorbents decreased realistic environmental concentrations of GLY to values that are below the maximum permissible value (0.1 μg/L) set out in the European Drinking Water Directive. When spiked wastewater samples were used, the magnetic nanosorbents at a dose of 2.5 mg/ml removed 76.8% of the GLY (initial concentration of 3.0 μg/L), demonstrating the potential application of these particles in aqueous matrices of complex nature. A more systematic investigation was conducted to study the adsorption performance towards GLY by varying several operational parameters in ultra-pure water, such as initial pH, contact time, sorbent dose and initial GLY concentration. The good adsorption capacity of the magnetic nanosorbents was ascribed to the presence of trimethylammonium groups from trimethyl chitosan that interact electrostatically with carboxylate and phosphonate groups of GLY molecules (Figure 1). Our results indicate that assisted magnetic water remediation using recyclable trimethyl chitosan surface modified magnetic nanoparticles is an efficient method for the removal of glyphosate from real water samples and artificial water to meet water quality standards.

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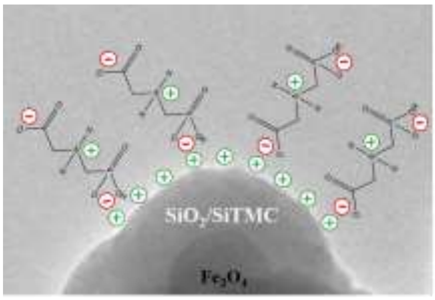

Figure 1: Schematic illustration of glyphosate species adsorbed onto Fe_3O_4@SiO_2/SiTMC nanosorbents dispersed in water.

Acknowledgments
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Proximity-Induced Quantum Interference Effects in Graphene

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Abstract

The study of quantum corrections to the conductivity in graphene with proximity-induced spin-orbit interactions is a challenging task due to the complex interplay between pseudo-spin (sublattice), iso-spin (valley), and real spin degrees of freedom. Recent studies [1,2] focused on the effect of weak spin-orbit coupling (SOC) and Gaussian matrix disorder. In this work we present a theory of weak localisation (WL) in graphene with large proximity-induced spin splitting exceeding the disorder-induced broadening of quasiparticles. We employ a self-consistent diagrammatic approach to sum the complete series of the maximally crossed diagrams, non-perturbatively in the SOC and Cooperon momentum, which allows us to access the regime of well-resolved spin splitting. Our theory is relevant relevant for graphene-transition metal dichalcogenides 2D heterostructures displaying strong WAL magneto fingerprints [3].

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The impact of novel high-performance substrates in ultrathin solar cells

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Silicon wafer-based technology dominated the photovoltaic market, with only a significantly smaller market share belonging to thin films. Ultrathin solar cells, using sub-µm absorbers are gaining relevance, due to their potential for savings in material resources and processing time, and potential for performance increase. The use of ultrathin absorbers to fabricate solar cells moves thin film technology to a relevant competitor status. The reduction of the absorber thickness down to the ultrathin range, raises two inherent intrinsic issues: increased rear interface recombination and decreased light absorption. These issues may be tackled through the incorporation of a dielectric passivation layer between the rear contact and the absorber [1]. Moreover, by having a very high percentage of the rear contact covered in a transparent dielectric layer for passivation in the contact structure [2], there is freedom to add extra functionality between the passivation and rear contact, leading to high-performance substrates (HPS). We will use Cu(In,Ga)Se_2 (CIGS) based ultrathin technology to showcase the optoelectronic potential of the HPS, and review some of the novel substrates architectures developed by the Nanofabrication for Optoelectronic Applications - NOA - group at INL. Optical simulations allow for accurate descriptions of the optical gains, providing a guideline to the passivation schemes. The NOA group has been focusing its investigation in: dielectric materials, innovative contacting approaches and industrially-friendly microelectronics-based nanofabrication (deposition, lithography, and etching) processes. The morphology, structure and optoelectronic properties of HPS and final devices are evaluated through advanced characterization techniques. We will discuss how the implementation of HPS can lead to increased figures of merit values over conventional ultrathin CIGS based devices. We will review the impact of lines vs. points contacts; the use of different dielectric materials and its impact on interface active defects density and built-in electrical field; and how highly reflective metals and nanostructures can be incorporated in HPS architectures to increase device's performance. Figure 1 shows three CIGS ultrathin solar cells, (a) with a conventional substrate and with a HPS based on two innovative contacting approaches schemes: (b) line and (c) point contacts. The implementation of novel SiO_x line contacts HPS in CIGS based devices, lead to improvements up to 5 % (abs) in the power conversion efficiency values over the conventional architecture.

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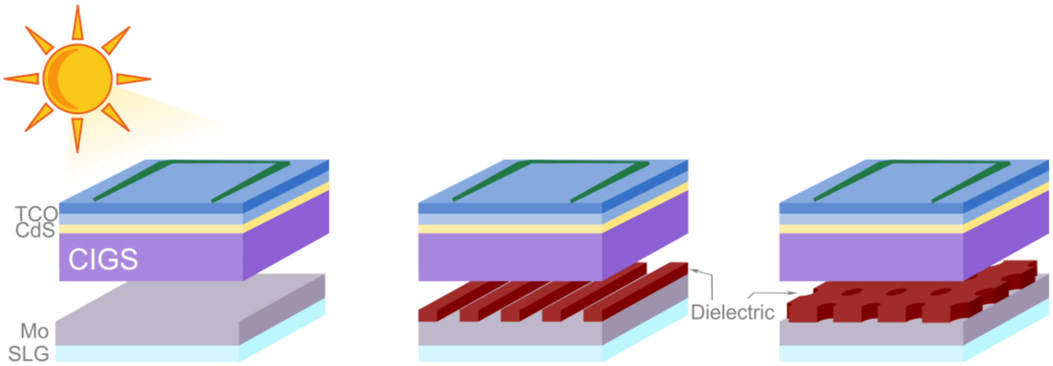

Figure 1: CIGS ultrathin solar cells with a (a) conventional substrate, (b) HPS based line contacts, and (c) HPS based point contacts.

Synthesis and functionalization of silver and gold nanoparticles for virus detection

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For the preparation of nanostructures which allow for the detection of adeno-associated virus (AAV) at different phases of development in insect cells, by Surface Enhanced Raman Spectroscopy (SERS), metal nanomaterials have been synthesized. In particular, plasmonic gold and silver nanoparticles (NPs) have been prepared in bare and functionalized forms. Gold NPs possess high biocompatibility and stability [1]. They are upon functionalization, appropriate for intracellular detection of AAV. Silver NPs, on the other hand, are cheaper to prepare, but typically more toxic. They are suitable for extracellular AAV detection, and as such they can be used in their 'bare' form. In addition, they can have a more general applicability, since they can have antimicrobial properties, and also used for chemical sensing [2].

In this work, different strategies for the synthesis of silver and gold NPs are presented, aiming at obtaining uniform structures with optimized plasmonic properties for SERS. The NPs are characterized by ultraviolet-visible (UV-VIS) spectroscopy, dynamic light scattering (DLS) and transmission electron microscopy (TEM). Thiol groups form strong metal-S bonds and allow for further functionalization of the NPs. They have been widely used to functionalize metal NPs for biomedical applications [3]. For our purpose thiol-functionalized gold NPs facilitate the attachment of antibodies and other groups (raman reporter group or cell penetrating peptides), which will allow indirect, intracellular detection of AAV. For this reason, we also report here the thiol-functionalization of the prepared gold NPs, following several functionalization strategies.

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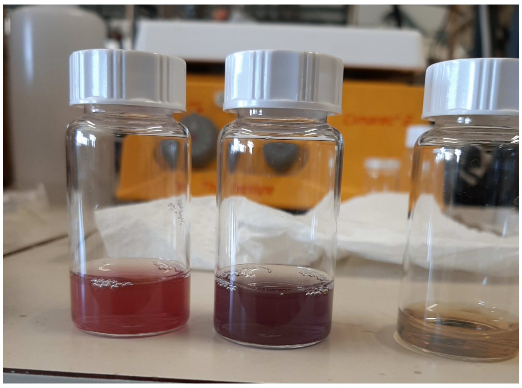

Figure 1: Gold (left and middle) and silver (right) nanoparticles.

Large-pore silica nanocarriers for antiangiogenic treatment against age-related macular degeneration

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The main cause of subretinal choroidal neovascularization in wet age-related macular degeneration (AMD) is an abnormal expression in the retinal pigment epithelium (RPE) of the vascular endothelial growth factor (VEGF).[1] Current AMD treatments present considerable issues that could be overcome by encapsulating anti-VEGF drugs in suitable nanocarriers with better penetration, higher retention times and sustained release.[2] The main objective of this work is the preliminary development of a drug delivery system for the topical administration of anti-VEGF siRNA molecules to RPE based on large-pore mesoporous silica nanoparticles (LP-MSNs). siRNA is loaded into LP-MSNs mesopores, while the nanoparticles' external surface is functionalized with polyethylenimine (PEI) chains that allow the controlled release of siRNA and promote endosomal escape to facilitate its cytosolic delivery.[3]

LP-MSNs were functionalised to obtain three different sets of materials. The first one, S1, was loaded with the fluorescent dye rhodamine B and capped with PEI chains, and allowed verifying PEI capping ability; S2 was covalently functionalised with rhodamine B isothiocyanate through 3-aminopropyltriethoxysilane chains, and externally capped with PEI, and employed to study nanoparticles cytotoxicity, cellular uptake and hemocompatibility; finally, S3 was loaded with anti-VEGFA siRNA and capped with PEI, and used for VEGF silencing in ARPE-19 retinal cells. Spherical monodispersed nanoparticles with an average size of 105 nm and center-radial pores of about 17 nm were obtained. The release studies showed that the cargo remains protected inside the pores in the absence of an adequate stimulus. The siRNA-loaded S3 reduced VEGF expression, demonstrating the developed nanocarrier capacity to provide siRNA protection, endosomal escape and consequent cytoplasmic release. Nevertheless, some issues were observed in cells viability.

Our results represent a first step for the development of topically administered nanovehicles based on LP-MSNs for the sustained attenuation of VEGF in the RPE by siRNA delivery systems. The successful results obtained in VEGF silencing in ARPE-19 cells demonstrate that although further modifications are needed for improving their biocompatibility, the designed nanodevices present a great potential for nucleic acid delivery, holding great promise for the next stages of the project.

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FIGURES

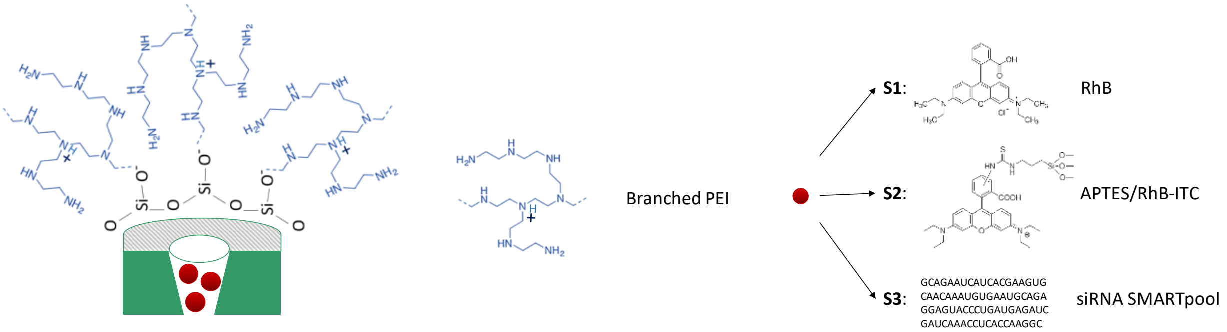

Figure 1: Schematic depiction of the synthesized nanodevices. siRNA is loaded into the mesopores, while positively charged PEI chains are attached via electrostatic interaction to the negatively charged silica surface.

Development of supramolecular peptide-based magnetolipogels: towards on-demand drug delivery

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Abstract

On-demand release remains a challenge in controlled drug delivery. Thermosensitive magnetoliposomes enable the magnetically-triggered release of both hydrophilic and hydrophobic drugs. The combination of magnetoliposomes with hydrogels afford magnetolipogels, where the former provides a reservoir for drugs and the hydrogel allows the immobilization of components [1]. The presence of magnetic nanoparticles allows the use of complementary strategies, mainly drug delivery, magnetic resonance imaging and hyperthermia [2]. Here, solid and aqueous magnetoliposomes were encapsulated in supramolecular naproxen *N*-capped dehydrodipeptide-based hydrogels (figure 1). Fluorescence spectroscopy was used to assess the dynamics of magnetoliposomes during gelation through co-encapsulation of Nile Red and curcumin. The final localization environment of encapsulated molecules was demonstrated to be independent of the magnetoliposomes architecture and of the used hydrogel. Hereby, the supramolecular peptide-based magnetolipogels are promising materials for future developments as it allows the independent modification of each component, so to optimize the system according to the required conditions.

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FIGURES

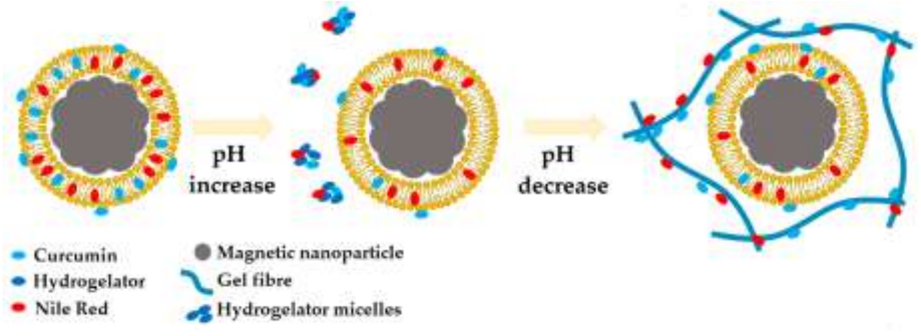

Figure 1: Scheme of the proposed process of incorporation of solid magnetic liposomes (SMLs) containing curcumin and Nile Red in a supramolecular naproxen *N*-capped dehydrodipeptide hydrogel activated through GdL induced slow pH decrease. Both Nile Red and curcumin released from the SMLs upon combination with the basic pH hydrogelator solution, and accumulated in the hydrophobic cavities of the hydrogelator micelles. Both molecules localized to hydrophobic cavities of the hydrogel matrix and the SMLs membrane once the gelation was triggered through pH decrease.

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Prediction of Purely Interfacial Giant Antidamping Spin-Orbit Torque induced by Skew Scattering

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Spin angular momentum transfer between conduction electrons and localized magnetic moments gives rise to interesting nonequilibrium spin-orbit coupling phenomena, including current-induced antidamping spin-orbit torque (ASOT), considered to be a crucial ingredient in next-generation spin memories [1]. In this talk, we present a new microscopic framework that accounts for intrinsic and extrinsic transport effects on equal footing and nonperturbatively, for the first time [2-3]. Calculations performed for generic **k·p** models of Rashba interfaces discloses a ubiquitous (yet hitherto neglected) mechanism for the generation of prominent interfacial ASOT: *skew scattering* activated by the out-of-plane tilting of spin-orbit textures in **k**-space. Our findings show that current-carrying Rashba interfaces can exert strong ASOT even in the absence of magnetic scattering centers and bulk spin-orbit-coupled transport mechanisms.

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Nanofabrication process for ex- and in-situ TEM heating and biasing chips

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Abstract.

In-situ transmission electron microscopy is a powerful technique which allows performing experiments in real time with atomic resolution thereby enabling to correlate, structural and compositional characteristics of materials with their physical properties.[1, 2]

In the current work, we present a process to fabricate heating and biasing chips in order to correlate ex-situ and in-situ transmission electron microscope (TEM) studies. Unlike the commercial chips, [3] ours do not have a SiO_2 or Si_3N_4 support membrane, but a trench for the electrons to pass through. The membrane absence helps avoiding problems related to their poor mechanical properties (brittleness). It also enables their use in liquid or atmospheric pressure environments, as well as high voltage bias measurements or studies at high temperature.

In addition, one of the most promising aspects of these chips is their ability to be used as a sample support in other analytical tools such as: electrical probe station, scanning electron microscope (SEM) or atomic force microscope (AFM), Raman spectroscopy, etc. This means that we can correlate different characterization techniques on a same nano-object.

In this talk, we will discuss the fabrication as well as the application of these chips into 1D [4] and 2D samples.

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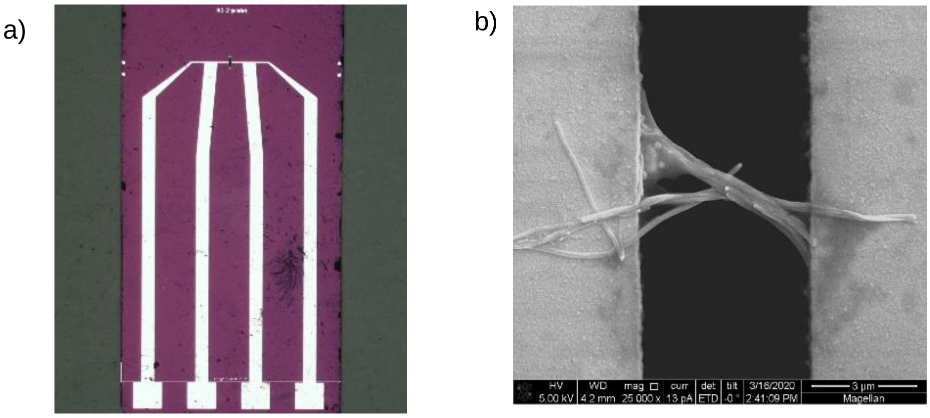

Figure 1: Optical a) and SEM Images b) of a 2 point-probe home-made chip. b). SEM image of drop-casted carbon nanotubes between electrodes

Abstracts Flash Poster

Simple one-pot separation of histidine-tagged proteins using NTA-functionalized gold nanostars

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Abstract

Nanoparticle-based protein separation methods rely on a specific interaction between a target protein and a ligand, and a way to specifically separate it from the medium. In this sense, magnetic nanoparticles are normally employed based on their ability to be specifically separated using a strong magnetic field. This Project is a follow-up based on previous published work by our research group using magnetic Ni-NTA coated gold nanostars (AuNS) for protein purification [1]. However, considering that magnetic gold nanostars are difficult to synthesize and require a magnetic component, this work focus on the development of an easier method for protein separation using centrifugation, targeting histidine-tagged proteins. As a proof of concept, histidine-tagged *Pf*HRPII (his-*Pf*HRPII), a histidine rich protein present in the blood of patients infected with malaria, was chosen as target, with the objective of purifying it by solely using a centrifugation procedure. To achieve that, Nickel-Nitrilotriacetic Acid (Ni-NTA), was employed as capping agent and ligand based on its specific interaction with histidine tags. Recombinant protein expression was performed in *E. coli* BL21 (DE3) transformed with a pET-his-*Pf*HRPII construct and induced by IPTG. Gold nanoparticles were synthesized and used as seeds to produce gold nanostars by a seed-mediated growth method adapted by Yuan et al. [2]. Nanostars were functionalized with Ni-NTA and 11-Mercapto-1-undecanol (MU), (AuNS-Ni-NTA-MU) and were used to purify his-PfHRPII from cell lysate. Nanostars functionalized with 11-Mercaptoundecanoic acid (MUA) (AuNS-MUA) were used as a negative control. Average nanoparticle concentration was accessed by Nanoparticle Tracking Analysis, and their UV-Visible spectra were analyzed to evaluate the quality of the synthesis. Agarose gel electrophoresis was used to evaluate the functionalization yield. Molecular weight and purity of the recombinant protein were accessed by SDS-PAGE. The purification procedure using AuNS-Ni-NTA-MU showed promising results when compared to a negative control of AuNS-MUA, and a high percentage of contaminants were removed. Colorimetric and Surface Enhanced Raman Spectroscopy (SERS) assays using gold nanostars-based detection on Western transfers are underway to evaluate the presence of the purified his-*Pf*HRPII. Once completed, this work will make possible both a expedite purification procedure and facile detection of histidine-tagged proteins by membrane staining and SERS.

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Optimization of drug-free nanostructured lipid carriers (NLC) for *Helicobacter pylori* eradication

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Helicobacter pylori (Hp) is a gastric pathogen that colonizes approximately half of the world´s population (ca. 4 billion people). Hp is responsible for the development of several gastric disorders, including gastric cancer [1]. The main treatments against Hp infection consist in the administration of antibiotics and proton-pump inhibitors. However, these treatments are failing, due to the increase of antibiotic resistance [2]. Drug-free nanostructured lipid carriers (NLC) have been studied for Hp eradication, showing a bactericidal effect against Hp both *in vitro* and *in vivo* [3,4,5]. However, eradication in mice was only achieved in 50% of the animals [5]. The main aim of this work is to optimize NLC efficiency by fine-tuning its physicochemical characteristics, in order to achieve full Hp clearance.

For NLC preparation, three surfactants were tested: Tween®60, Tween®80 and Cetyltrimethylammonium bromide (CTAB). NLC were prepared by hot homogenization followed by ultrasonication. For optimization purposes different sonication parameters were tested. The NLC were characterized in terms of size distribution and surface charge by dynamic light scattering (DLS) and electrophoretic light scattering (ELS), respectively. Nanoparticle concentration was measured by nanoparticle tracking analysis (NTA). Additionally, in NLC with Tween®60 and Tween®80 the effect of dialysis was evaluated. Dialyzed and non-dialyzed NLC were tested *in vitro* against Hp J99 strain.

All NLC were optimized in terms of size by altering the sonication parameters. The nanoparticles with Tween®60 and Tween®80 varied in a range of 200-430nm and 190-230nm, respectively. In terms of charge both NLC were anionic with a surface charge between -25 to -30mV. Cationic NLC with CTAB and a mix of Tween®60/CTAB had sizes from 107 to 200 nm and a surface charge around 25 and 76 mV. All NLC stocks had a final concentration in the range of 10^{14} particles/ml. NLC with Tween®60 and Tween®80 were tested against Hp J99. After 24h of incubation, both NLC formulations had similar outcomes, achieving a bactericidal effect. Non-dialyzed and dialyzed NLC showed also the same bactericidal activity. Moreover, when testing NLC with slightly different sizes smaller NLC showed less effect.

The NLC were successfully optimized in terms of size and charge. The formulations with Tween®60 and Tween®80 were effective against Hp, and the dialysis didn't affect the NLC bactericidal activity. Preliminary results indicate that size can play a role in the NLC bactericidal activity. These results support the therapeutic potential of these nanoparticles.

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Photoreduction: new strategies for Additive Manufacturing

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Abstract

In the industry 4.0 framework, Additive Manufacturing (AM) together with 3D printing techniques have emerged as promising processing methods and caught the attention of research investment especially for nanotechnology applications.

The DLW is an Additive Manufacturing (AM) technique for micro and nano-fabrication and here we're going to analyze a particular novel technique that allows to realize metallic structures onto solid substrates at the sub-micron scale: the two-photon photo-reduction of photosensitive metallic precursors.

Infact Additive Manufacturing combined with the Two Photon Absorption process allowed to create 3D-complex objects taking advantage of the photo reduction of the gold precursor (tetrachloroauric acid, HAuCl4) and the femtosecond pulsed NIR Erbium laser (λ = 780 nm).

A comparison with another AM technology as the stereolithography (SLA) could be, it will be interesting to test peculiarity and features of the various techniques and to choose the most efficient, easy and rapid one. In this case a different substrate (acrylic resin) is used to obtain nanostructures (AuNPs) onto it.

We pointed out the importance of the diffusive process for the created nanoparticles (NPs) growth and the necessity to have a polymeric network (polyvinyl alcohol, PVA) in order to "held" the NPs at their place, thus preventing their free diffusion. As the writing process occurs at the interface with the solid substrate, it is mandatory for the last to be optically accessible. In this new study, we preferred natural hydrogel matrices (isinglass, agarose gel), compared to PVA, keeping an eye open on the green chemistry and featuring a good transparency at the used wavelength. Moreover, a better control on the ionic concentration led to an important improvement of the created structures quality (Figure 1).

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FIGURES

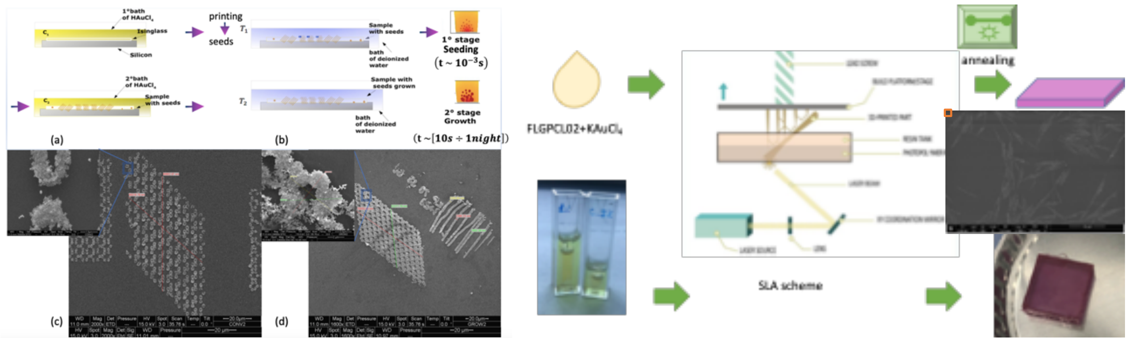

Figure 1: (a) A sketch of the of the experiment: the first bath in HAuCl4 of the silicon substrate after the spin-coating deposition of the isinglass on it and the second bath in the gold precursor to control the growth (size of GNPs: 40÷70 nm); (b) the subsequent deionized water baths to remove chloroauric ions and to stop the growth respectively. SEM images and their magnifications of some points nanostructures before (c) and after (d) the growth. On the right the scheme of the SLA technique and a SEM image of the gold NPs created inside the resin.

Controlled design of gold-based hybridnanomaterials with core-shell architecture

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Keywords: Gold-based nanoparticles, core-shell structure, metal-semiconductor junctions, plasmonics.

Gold-based nanoparticles have been the subject of intense research due to their versatility and potential use in a wide variety of application fields such as plasmonic photocatalysis, plasmon-enhanced spectroscopy or Nanomedicine. Gold at the nanometric scale possess unique optical and catalytic properties that can be further boosted when combined with other metal or oxides to form multifunctional heterostructures. Bimetallic structures can be formed by combining gold with other noble metals such as platinum, silver, or palladium. Metal-semiconductor hybrid structures can also be generated where gold interacts with different semiconductor oxides such as copper or titanium oxides. These novel hybrid materials exhibit synergistic properties that may overcome their individual counterparts. There are multiple strategies to combine and and maximize the interaction of these heterostructures. Herein we present a variety of synthesis approaches using wet chemistry to build multiple core-shell nanoconfigurations. Core-shell structures emerge as one of the most attractive alternatives where the gold core interacts as much as possible with the outer shell. The design and good understanding of these structures is essential to obtain hybrid materials with a targeted optical and catalytic response that can be potentially envisioned for an extensive number of environmental and biomedical applications. We have explored a good number of variables to tune and maximize the characteristics of core-shell gold-based hybrid nanoplatforms. Morphology, pore size, shell thickness or crystallinity of the sample are fundamental parameters to take into account if you pretend to build well-designed core-shell structure.

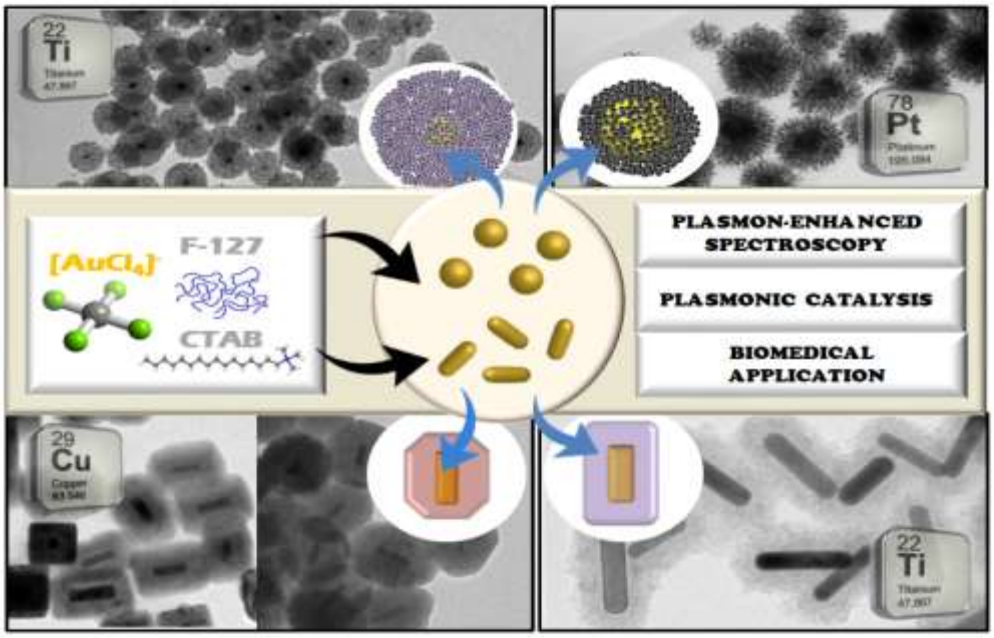

Figure 1: Selection of gold-based core-shell plasmonic configurations

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Anticancer Activity of Carbon Nanomaterials-Camptothecin Complexes

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Due to their large surface area, high cellular internalization and preferential tumor accumulation, carbon nanomaterials have attracted much attention in biomedicine to be used as drug nanocarriers to transport chemotherapeutic [1-3]. Furthermore, these systems could be used for formulation of hydrophobic molecules which lack of suitable physicochemical characteristics required for development of stable pharmaceutical dosage form. Camptothecin (CPT) is a more potent anticancer agent than other well-known anticancer drugs such as doxorubicin (DOX). However, CPT practical use is greatly hampered due to its low solubility in biological media, so developing new drug delivery nanocarriers for CPT would be of high interest [4]. In this work, the potential of carbon nanotubes (CNT), graphene oxide (GO), reduced graphene oxide (RGO) and carbon nanodiamonds (ND) in the field of drug delivery as nanocarriers of CPT was compared. *In vitro* studies were performed on human epithelial colorectal adenocarcinoma (Caco-2) cells. The highest improvement in CPT anticancer activity was obtained for nanocarriers that are able to establish strong π-π interactions with CPT [5].

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The effect of graphene reinforcement on the properties of TiO_2

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Abstract

The effect of graphene nanoplatelets (GNP) reinforcement on the microstructure and mechanical properties of the titanium dioxide matrix composite was studied. For this purpose, TiO_2 matrix composites with various reduced graphene oxide (rGO) concentration of 0, 0.5, 1, and 2 wt% were sintered by spark plasma sintering (SPS) at the1200°C during 5 minute holding time and under 90 MPa pressure. Graphene oxide was mixed with TiO_2 by ultrasonical excitation for 2 hours, leaded by temperature treatment at 300°C -30 min in vacuum environment. Process was accomplished by graphene oxide reduction at 300°C. Conducted process gave uniform distribution of GNP layers in the TiO_2 matrix and covered each particle of titanium dioxide with graphene nanoplatelets. Microstructure and mechanical properties of sintered samples were investigated. The fractured-sectional SEM images of processed samples showed that porosity slightly increases depending on concentration of GNPs. Hardness and fracture toughness were investigated after Vickers indentation analysis. Electrical resistivity measurements were performed by the two-probe method. Resistance measurement was done in two orientations of the samples, perpendicular ($\sigma\perp$), and parallel ($\sigma||$) to the SPS pressure axis, because of the specific anisotropic nature of the graphene and SPS densification.

Charts presented below as a figure 1 shows Hardness (a), fracture toughness (a) and electrical conductivity (b) values depending on concentration of GNPs. Graphene takes an important role in the prevention of grain growth as well as acting as the barrier for crack propagation and increasing its fracture toughness. Maintained microhardness and 4.5 times increased fracture toughness revealed the advantage of composite with 1wt% of GNPs compared to pure TiO_2. The higher conductivity occurs for all samples in the perpendicular direction due to the TiO_2 crystalline and morphologic textures formed by uniaxial pressing applied during the sintering. Pure TiO_2 shows approximately10 times lower conductivity with comparison to the samples with 1wt % of GNPs. In parallel measurement for 0.25 and 0.5wt%, GNPs additive slightly improves the conductivity of pure TiO_2 but not at the same rate as in perpendicular measurement. The percolation threshold was obtained between 0.5wt% and 1wt% GNPs where the conductivity jumps up from 1 to 9 S/m (Fig. 1b). It turned out that 1wt% GNPs is already a sufficient amount to fill up around the matrix grains, affect the electrical conductivity and acquire 23 times higher conductivity for pure TiO_2 ceramic.

FIGURES

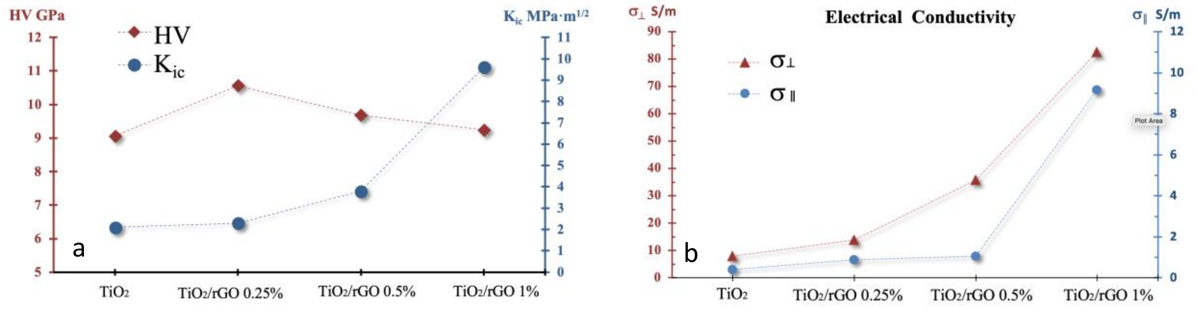

Figure 1: Chart of (a) HV, fracture toughness and (b) electrical conductivity of TiO_2 ceramic with the dependence of GNPs concentration

Oxygen assisted monocrystalline graphene growth by chemical vapor deposition

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Monocrystalline single layer graphene is an appealing material for applied research due to its exceptionally large carrier mobility - a key parameter for most applications in electronics - and strong THz optical response, for photonic applications**.** However, for an industrial scale exploitation of these properties, it is necessary to obtain high quality graphene by scalable means, e.g., by chemical vapour deposition (CVD) [1]. For single layer graphene growth it is preferable to use copper instead of, for example, nickel substrates due to the low carbon solubility in copper [2]. The number and size of the graphene crystal grains is, in a first approximation, determined by the copper substrate characteristics. Therefore, it is necessary to treat the high-purity copper for control of its cleanliness, oxidation state, and roughness. . Substrates were treated in an ultrasonic bath with an acidic solution of HCl and $FeCl_3$, followed by oxidation in air (hot plate) at 180ºC for 30 minutes. Keeping an extended oxidized surface is key to obtain very low nucleation density, providing graphene crystals of large size and good quality. For graphene growth, the copper substrates were enclosed in a graphite confinement box to increase growth rate [3] while protecting the sample from silicon oxide and other contaminations coming from reactions with the quartz walls of the reactor. A secondary height-controlled sapphire cavity is used to accommodate the substrate inside the primary graphite cavity and release in situ trace amounts of oxygen that keep the Cu substrate oxidation level, and further increase growth rate and reduce nucleation density. The consistency in this step is fundamental to achieve a good reproducibility of the results. Samples are characterized by microscope inspection for flake size and morphology, after which they are transferred onto Si/SiO_2 substrates, using the wet polymer transfer process, for Raman spectroscopy analysis.

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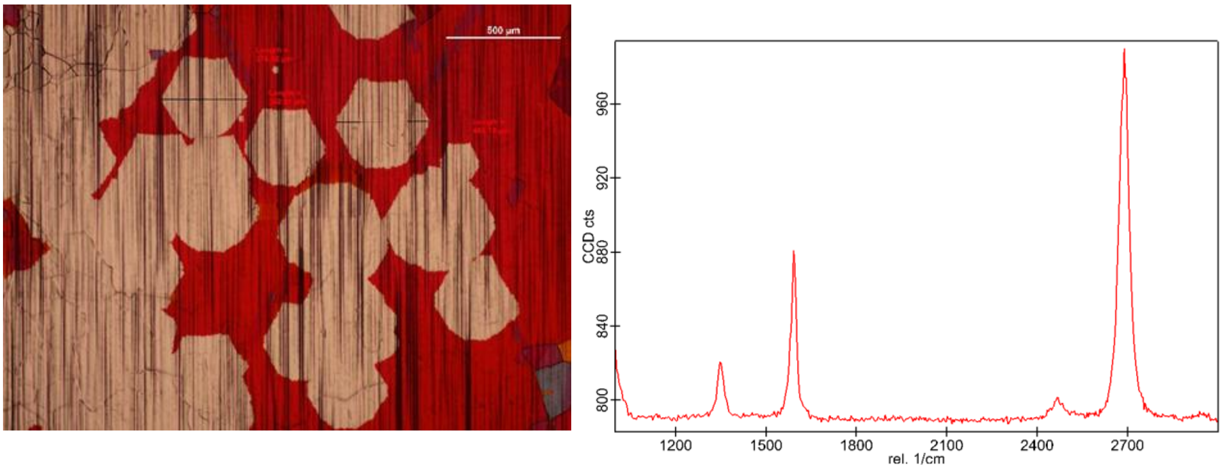

Figure 1: Hexagonal graphene flakes (left) with 400 µm diameter and Raman spectrum of transferred graphene (right).

Upscaling $MoSe_2$ and hBN via controlled chemical vapor deposition

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Two-dimensional materials (2DM) are a topic of high interest in the materials science community to engineer innovative devices. Among them, hexagonal boron nitride (hBN), an insulator with structure similar to graphene, is an optimal candidate to serve as insulating/passivation layer in graphene-based devices, enabling high carrier mobilities [1]. Semiconducting 2DMs have shown outstanding optoelectronic properties, such as thickness-dependent photoluminescence, combined with lightweight and flexibility [2, 3]. In particular, atomically thin MoS_2 and $MoSe_2$ have been proposed and applied in several electronic devices [4]. Notwithstanding a considerable effort, a production method for 2DMs that would guarantee large scale, high throughput and low cost is still lacking. Chemical vapor deposition (CVD) is perhaps the most promising route for the batch production of 2DMs with high quality, but a few crucial challenges need to be addressed to attain cost-effective and reproducible processes over large areas. In this work, we report the growth of atomically thin $MoSe_2$ and hBN by atmospheric-pressure CVD. The samples were evaluated by electron microscopy and atomic force microscopy, as well as Raman and X-ray photoelectron spectroscopy. We adopted two different paths for the growth of $MoSe_2$ on two substrates (*i.e.*, soda lime glass and SiO_2), using Se powder and Mo foil or Mo powder as solid precursors (Figure a). By tuning the process parameters, i) monolayer $MoSe_2$ flakes with large area were grown on glass which showed intense photoluminescence at ~1.57 eV (Figure b) and ii) continuous polycrystalline $MoSe_2$ films were grown on SiO_2. By comparing samples grown in the same conditions on the two substrates, we studied the mechanisms involved in the processes. The 2D $MoSe_2$ materials can be integrated in optoelectronic devices, such as photodetectors, taking advantage of their high photo-responsivity. hBN was grown on Cu foil and transferred to SiO_2 via wet-etching method. We obtained continuous hBN samples with areas up to several cm^2, keeping the thickness within 5 nm (Figure c).

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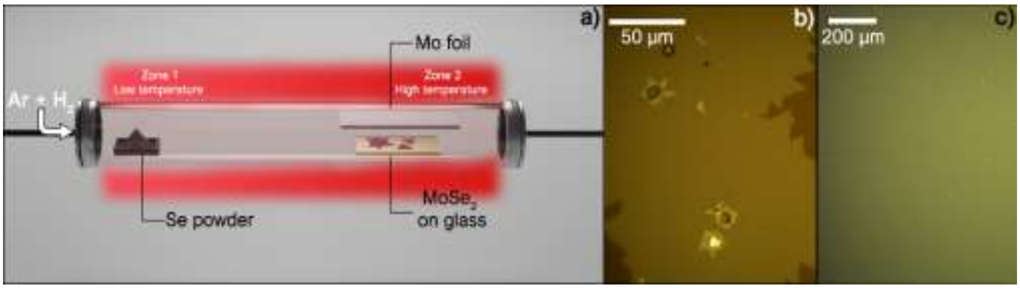

Figure 1: *a) Schematic of the CVD setup for $MoSe_2$ growth;* b*) Optical image of $MoSe_2$ deposited on glass; c) Optical image of CVD-grown hBN continuous film transferred to SiO_2.*

Abstracts ePoster

Towards the development of dual-responsive composites for simultaneous hyperthermia and chemotherapy

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Abstract

There is an urgent need to develop more effective therapies to fight cancer. Nanotechnology-based approaches are a possible route to perturb tumour's biology and deliver therapies. Hyperthermia is an emergent therapeutical strategy as tumour cells are more susceptible than "normal" cells to rises in temperature. One of the biggest challenges in hyperthermia is the induction of local heating in deep tumours, being magnetic nanoparticles a potential route to achieve this goal. Previously, we incorporated iron oxide nanoparticles (Fe_3O_4-NP) with thermo-responsive polymers for simultaneous hyperthermia and *in situ* delivery of chemotherapeutic drugs (Doxorubicin) [1]. We are now applying this approach to a novel cationic thermo-responsive copolymer, AEtMA-Cl/DEAEA (1:3 ratio), possesses excellent properties suitable for long-term cell culture [2,3]. Here, we aim to produce nanocomposites of AEtMA-Cl/DEAEA containing Fe_3O_4-NP for combinatory chemotherapy and hyperthermia. To produce fibrous composite, we have successful obtained poly-AEtMA-Cl (PAEtMA-Cl) by RAFT and making fibres using electrospinning. PAEtMA-Cl was successfully electrospun together with poly(ethene glycol) (PEO) as observed by atomic force and optical microscopy. By electrospinning, we obtained PAEtMA-Cl fibres that ranged (1-9 μm) diameter. As predicted, PAEtMA-Cl/PEO nanofibers are soluble in water. In order to use PAEtMA-Cl/PEO for cell culture, we are investigating different crosslinking strategies – covalent and ionic. Preliminary data shows that multivalent anions such as sodium tripolyphosphate (TPP) leads to the formation of porous networks of PAEtMA-Cl in aqueous solutions (Fig. 1), so we will use it to crosslink nanofibres. In addition, we observed that TPP can be used to form soft microgels, which may in future provide a novel material for drug delivery applications. In summary, we have demonstrated that PAEtMA-Cl can be electrospun and processed as microgels. This will allow us to produce a novel dual-responsive magnetic nanocomposite for cancer applications.

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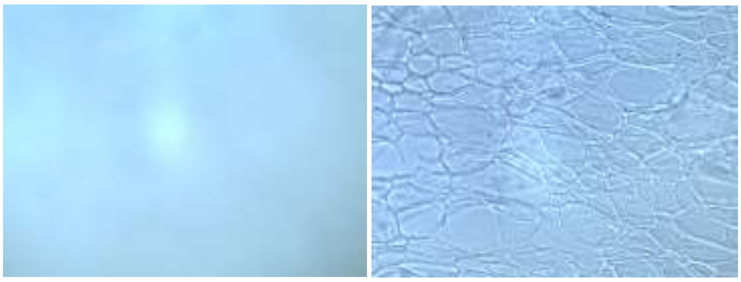

Figure 1: Representative bright field image of PAEtMA-Cl in water (a) crosslinked with TPP (b). Total Magnification = 400x.

Improving the mechanical performance of HDPE employing dendrimer-like silica nanospheres and halloysite natural nanotubes as promising nanofillers through *in-situ* polymerization

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Polyolefin nanocomposites, and more specifically, polyethylene/inorganic oxides nanocomposites are promising materials that combine the ductility, flexibility and easier processibility of their polymer matrix with the stiffness and rigidity of their inorganic filler. The main challenge in preparing these nanocomposites is achieving a suitable compatibilization of the interfacing components, as the hydrophilic nature of the inorganic filler results in a tendency for the nanoparticles to aggregate and thus reduce the reinforcing effect. There are several techniques to prepare nanocomposites, out of which *in-situ* polymerization provides a good dispersion of the filler. In this study, we report the synthesis of HDPE nanocomposites via *in-situ* polymerization reinforced with dendrimeric silica nanospheres (DS) which has previously proved a promising support for metallocene catalysts in ethylene polymerization, and natural halloysite nanotubes (HNT), a cost-effective and naturally abundant aluminosilicate which presents a tubular morphology. The polymerization reactions were performed by preparing a heterogeneous catalyst made up of a zirconocene catalyst immobilized onto MAO-pretreated supports (DS-MAO and HNT-MAO). A reference non-reinforced HDPE was prepared via solution polymerization with the homogeneous zirconocene. The materials were characterized regarding the polymer's crystalline features, morphology, and filler dispersion. The mechanical reinforcement of the nanocomposites was assessed by stress-strain measurements and compared against the remaining properties. We observe both fillers present good dispersion within the polymer matrix, as well as high crystallinity of the matrix. We obtain highly reinforced nanocomposites regardless of the filler employed, with increasing stiffness proportional to the filler content. Remarkably, the limit properties of the nanocomposites do not decrease significantly with reinforcement content, in some cases retaining the elongation at break values of pristine HDPE.

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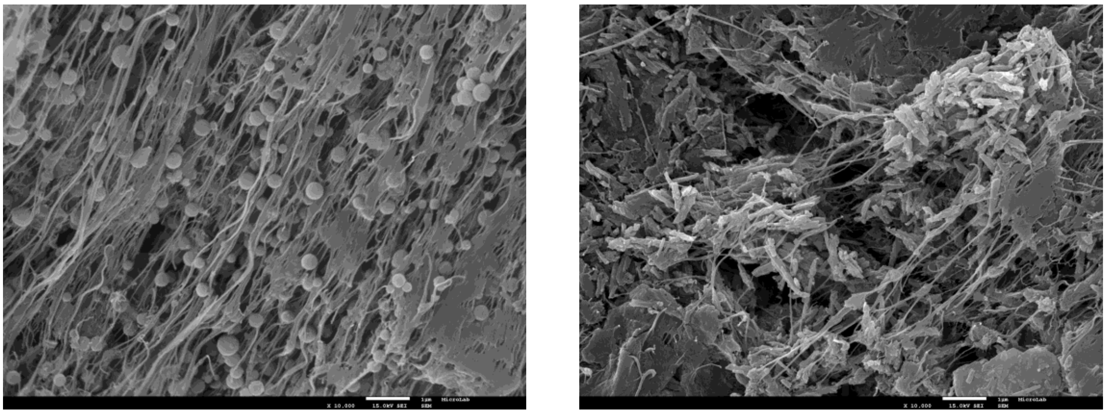

Figure 1: SEM micrographs of DS (left) and HNT (right) dispersed within the HDPE matrix.

Exploring Graphene-Based Materials As New Nanofillers To Reinforce Poly(Ethylene Glycol) Hydrogels For Load-Bearing Applications

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ABSTRACT

Poly(ethylene glycol) (PEG) hydrogels are biocompatible and highly resistant to protein adsorption, serving as a “blank slate” with tunable physicochemical properties. However, hydrogels are typically very weak, preventing their use in load-bearing applications, e.g. for cartilage, intervertebral disc, blood vessels or cardiac valves. Several strategies have been proposed for their mechanical reinforcement, such as the incorporation of nanofillers [1].

Graphene is a single-layer honeycomb lattice of sp2-bonded carbon atoms with outstanding stability, mechanical and electroconductive properties. It is the thinnest yet strongest material ever measured [2]. Graphene-based materials (GBM), particularly oxidized forms – which are reportedly less cytotoxic than reduced ones [3] – have been proposed as nanofillers for hydrogels [4, 5].

The goal of this work is to explore the use of different GBM as nanofillers to reinforce PEG hydrogels, turning them into stiffer and stronger hydrogels. We aim to understand the influence of different GBM parameters, such as concentration, thickness, lateral size or oxidation degree, in the mechanical properties of PEG/GBM composite hydrogels.

Graphene oxide (GO) and few-layer graphene oxidized (FLGO) were synthesized from graphite powder and FLG, respectively, by modified Hummer’s method. According to XPS analysis, GO contained 30.2% of oxygen atoms, while FLGO contained 31.6% oxygen atoms, which confirms the oxidation of graphite and FLG, respectively. TEM images show GO sheets with a lateral size of < 3 µm, while FLGO sheets were ~5 µm large.

PEG/GBM composite hydrogels were produced by *in situ* crosslinking of a precursor solution containing PEG dimethacrylate macromers (8 kDa, 15 wt%) and different concentrations of dispersed GO, FLG or FLGO. Tensile tests show that composite hydrogels with ≥2 wt% GO are significantly stiffer and stronger than neat PEG hydrogels. The higher the GO concentration, the greater the stiffness and strength appear to be (in the 2-4 wt% range). The incorporation of 1 wt% FLGO in PEG hydrogels results in an increase of Young’s modulus from 17.9±4.4 kPa to 78.7±5.8 kPa. In fact, the tensile properties of 1 wt% FLGO hydrogels were comparable to those of 4 wt% GO hydrogels. FLGO sheets have a larger surface area with which PEG chains can interact, possibly providing more interface to transfer stress from the polymer network to the nanofillers (vs. GO sheets). Regarding the oxidation degree, FLG appears to not reinforce neat PEG hydrogels. The low oxidation of FLG prevents its interaction with PEG chains, as expected. The reinforcement is also greater when GO and FLGO are incorporated in the hydrogel’s precursor solution as a colloid than as a powder.

The development of such composites paves the way for the application of hydrogels as versatile as PEG in load-bearing tissues.

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Development of nanoplatforms for sers based on silver nanostars

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High-performance, low-cost and reproducible SERS platforms are critical for the application of this ultra-sensitive technique in numerous fields, including the detection of biological and environmental analytes. In this this work, we developed a low cost, ultra-sensitive homogeneous substrate based on borosilicate glass covered with silver nanostars (AgNSs) for indirect detection and quantification by surface-enhanced Raman spectroscopy (SERS)[1]. Similar substrates were proven to have a good performance in SERS, providing enhancement factors up to 10^4.[2,3] Substrate fabrication was performed by centrifugation of a colloidal suspension of AgNSs into the glass substrate. Optimization of the experimental conditions was performed by varying parameters such as (i) concentration of AgNSs, (ii) morphology of AgNSs, (iii) solvent. Colloidal stability and hydrodynamic diameter of the AgNSs suspensions was investigated by dynamic light scattering (DLS), electrophoretic light-scattering (ELS) and nanoparticle tracking analysis (NTA) showing zeta potential -35.5 ± 1.1 mV and hydrodynamic diameters of 83.0 ± 2.1 nm. The surfaces were characterized by scanning electron microscopy (SEM), with the best ones showing a homogeneous particle distribution on the surface (figure 1B). Until the present moment, tests using crystal violet as SERS probe showed an enhancement factor of 8.9×10^6 for the best substrate based on AgNSs with tip-to-tip length of ≈270 nm.

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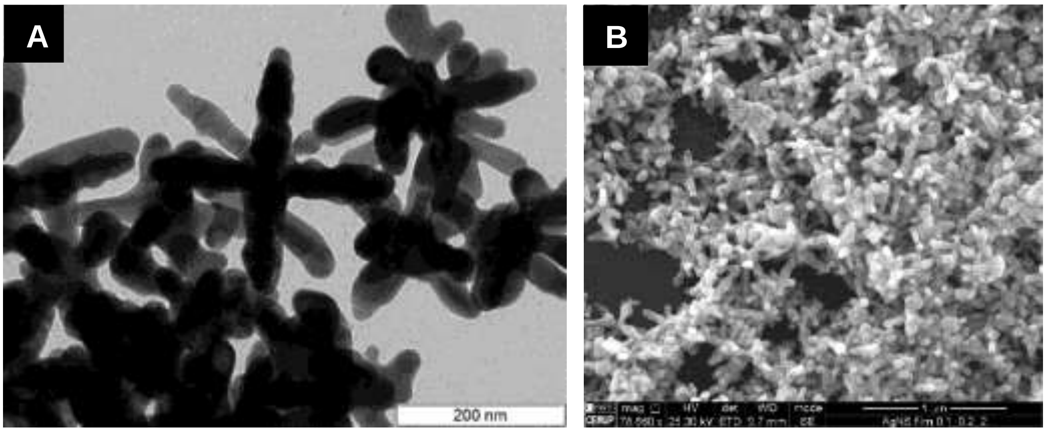

Figure 1: Transmission electron microscopy (TEM) micrograph of AgNSs (A) and scanning electron microscopy (SEM) micrograph of a SERS substrate (B).

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Iron effect on the oxidation, colour and antibacterial activity of zinc nanostructures for active food packaging produced by magnetron sputtering

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Keywords: Zinc-Iron, sputtering magnetron, nanostructures, oxidation, antibacterial test, colour, food packaging.

Zinc oxide nanoparticles are known as an antibacterial agent with a great variety of applications in the industrial field, especially in food packaging. Recently, it has been demonstrated that the mixed oxides from Zn (Zinc) and Fe (Iron) can be used as a pigment and humidity sensor **[1-3]**. Based on these applications, Zn and Zn-Fe nanostructures were produced to evaluate their colour and antibacterial properties during their oxidation when exposed to different ranges of humidity. Particular emphasis is placed on highlighting the effect of the Fe content on the functional properties.

Zn and Zn-Fe nanostructures were produced using two different methodologies, (i) a classical magnetron sputtering, and a hybrid system composed by a cluster gun and a magnetron sputtering. All depositions were performed in Ar atmosphere, varying the current density, from 0.1 to 0.5 A, and deposition time. The morphology and elemental analysis were evaluated by scanning (transmission) electron microscopy (SEM and STEM), energy dispersive spectroscopy (EDS) and Inductively Coupled Plasma (ICP). Colour measurements were carried out in a CM-2600d/MINOLTA spectrometer and the antibacterial tests were assessed by the zone of inhibition (ZOI) assay.

The samples were classified by thickness, Zn-Fe concentration/fraction, and morphology (NPs/film). Afterwards, the results demonstrated, a significant effect of the insertion of Fe in Zn nanostructures. Consequently, an increase of the fraction of Fe caused a lower L* value and a decrease of the antibacterial activity when compared to pure Zn nanostructures.

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LASER-ASSISTED CHEMISTRY TO DESIGN ADVANCED SINGLE-ATOM CARBON-BASED CATALYSTS

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Keywords: Metal single atom catalysts, carbon support, electrocatalysis, ORR catalyst.

Nowadays, the transition from combustion energy conversion technologies based upon the use of fossil sources to clean technologies, has driven a growing demand for the development of outstanding catalysts that radically change the current concepts of catalysis. Single-atom catalysts are recently emerging as a new frontier in heterogeneous catalysis science.[1] Especially, carbon-based materials have proven to be excellent candidates for supporting single-atom catalysts due to their unique structural and electronic properties. However, fabricating single-atom catalysts, providing 100% metal centers dispersion under synthesis and catalysis conditions are highly challenging. This work is set on the establishment of the laser pyrolysis processing as one-pot and up-scale alternative in the synthesis of a single-atom catalyst with multiple catalytic active sites $M-N_x$ (M= Fe) dispersed on a solid carbon support. Spatial uniformity and high temperature (> 500ºC) in the reaction zone, short millisecond scale residence times, and high heating/cooling rates are the most important advantages of this strategy to control uniform atomic-scale distribution of the metal atoms. The results suggested a promising route towards tailored generating of single-atom catalyst, which may enable a wide variety of applications since there are many possible combinations of metals and dopant atoms.[3] Finally, promising application~~s~~ of the as-prepared catalysts for oxygen reduction reaction (ORR) is described.

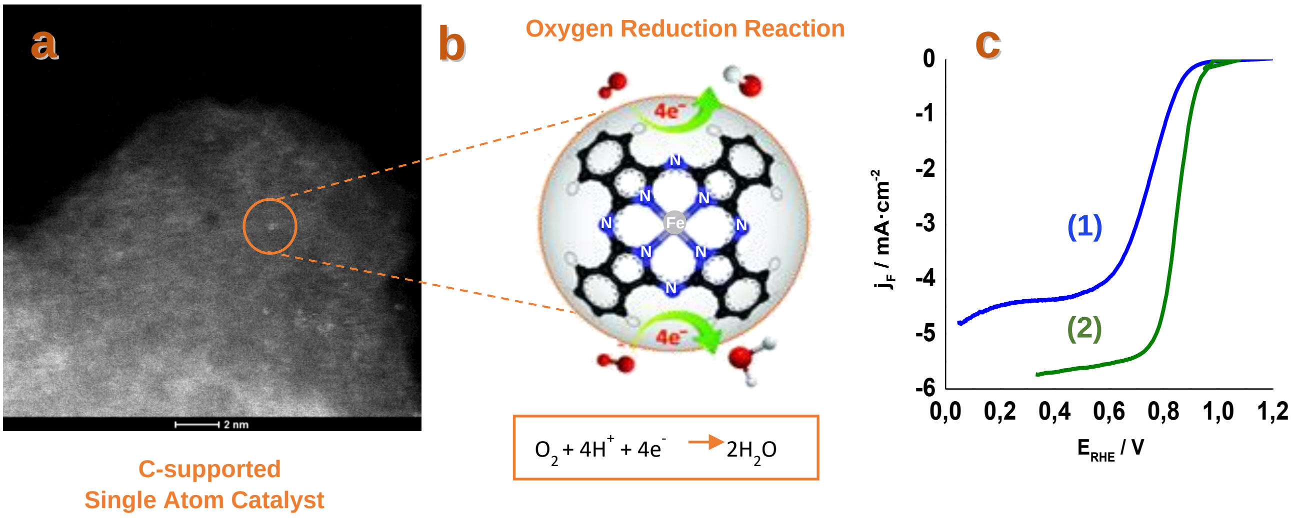

Figure 1. A) STEM image corresponding to Fe-N/C single atom catalyst, B) Detailed scheme of ORR reaction mechanism in the cathode of fuel cells and C) ORR polarization plots in 0,1M KOH of (1) Fe-N/C catalyst and (2) reference Pt/C catalyst. Test conditions: Disk rotation 1600 rpm, catalyst loading 0,6 mg/cm^2.

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New amperometric biosensor for determination of heavy metal ions based on the enzymatic inhibition of HRP immobilized on ferrocenyl polycyclosiloxane/Gold Nanoparticles modified electrode

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Heavy metals such as lead, copper, cadmium and mercury are non-degradable, cannot be detoxified biologically and can accumulate in the biosphere and transfer to the alimentary chain, thereby giving arise to potential serious health consequences for human beings, animals and plants [1]. We focuse on lead and cooper ions because they may reach the environment due to conscious or unconscious human activities. Lead common sources are the PVC pipes in sanitation, recycled PVC lead paints, etc. as well as the lead batteries, while the common sources of cooper are the fertilizers, tanning, and photovoltaic cells [2]. Both ions are related with adverse effects on the human metabolic process [3,4]. In the last years, the enzyme inhibition caused by heavy metals has provided a new way to develop inhibition-based biosensors [5]. For this purpose, horseradish peroxidase (HRP) is one of more used enzymes due to their low cost, availability and easy immobilization. In addition, the incorporation of AuNPs in biosensing devices has found to improve the electrode surface and the electronic conductivity, since the AuNPs enhance the transfer of the electrons generated by the enzyme-catalyzed redox reaction to the electrode surface [6]. Furthermore, the AuNPs present a high biocompatibility with the enzyme Horseradish peroxidase (HRP) maintaining their bioactivity [7]. Based on our previous experience, here we present the first results obtained with an amperometric hydrogen peroxide (H_2O_2) biosensor developed by covalent immobilizing of HRP onto AuNPs electrodeposited from a ferrocenyl polycyclosiloxane, also electrodeposited film on a Pt electrode [8]. The biosensor show direct electrochemistry with the HRP and now is being successfully applied to the indirect determination of Pb^{2+} and Cu^{2+} based on the inhibition of the enzyme, with linear ranges of 0.05-0.7 mgL^{-1} and 0.05-1.20 mgL^{-1}, respectively, and a K_I 1.7 mgL^{-1} for the non-competitive inhibition of Pb. the rest of the study is being completed and its results will be displayed on the poster presented at the conference.

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FIGURES

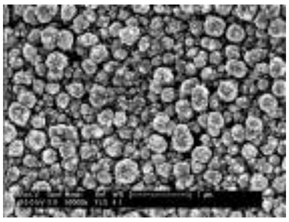

Figure 1: SEM image of the electrode surface previous to enzyme immobilization

Silver Nanostar-based Biocide Surfaces

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Nosocomial infections are a major concern given the current multiple resistance to antibiotics developed by the involved bacteria. Bacterial pathogens can grow in surfaces and eventually form biofilms, that adds an extra layer of complexity to fight their proliferation. [1] This way, inhibiting the proliferation of such microorganisms on surfaces is the first step for material's safety. The effect of silver ions (Ag^+) as a bactericidal agent is well known [2], so in this work we used silver nanoparticles as a "reservoir" of Ag^+, in the form of silver atoms (Ag^0) that comprise the nanoparticles and, when oxidized, can leave the particle as Ag^+. In this work, we covered 0.13-0.16 mm thick, 9 mm diameter glass disks with silver nanostars (AgNSs) using a deposition by centrifugation method [3]. The silver nanostars were synthesized as described elsewhere [4], with modifications. The resultant silver nanostars presented a 186 nm mean hydrodynamic diameter (distribution in number, determined by nanoparticle tracking analysis). After the deposition of the AgNSs, the surfaces were characterized by scanning electron microscopy, showing a homogeneous distribution of AgNSs across the surface. The proliferation of two bacterial species – *P. aeruginosa* ATCC 27853 and *S. aureus* ATCC 25923 – was accessed by several methods, including LIVE/DEAD cell viability staining assays, by fluorescence confocal microscopy. In figure 1, it is possible to see, for *S. aureus* ATCC 25923, viable microorganisms on top of a non-coated surface (stained as green, left), whereas for the AgNSs-coated most of the bacteria were non-viable (stained as red, right). The AgNSs described in this work showed a good potential as a surface coating with biocide effects.

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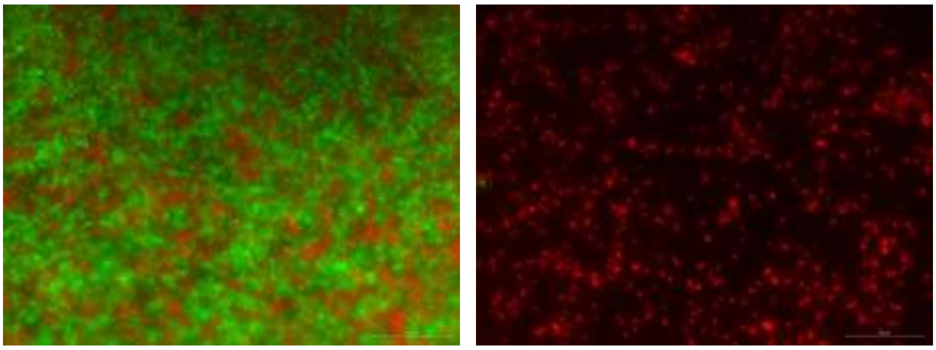

Figure 1: LIVE/DEAD staining micrographs of *S. aureus* ATCC 25923 deposited on non-coated (left) and AgNSs-coated (right) surfaces, after 24 h.

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Complex Liposomes for Phototherapy: development and optimization

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Photodynamic Therapy (PDT) is currently a promising treatment methodology for several types of cancers [1]. Three main components are necessary for PDT: a light source, a photosensitizing molecule and oxygen [2]. Under these conditions, PDT leads to oxidative stress and, as consequence, cell death. However, drug solubility and its delivery to the target tissue are factors that can affect the treatment efficacy. To overpass these situations, it is possible to use nanocarriers such as liposomes. These lipid carriers are able to encapsulate both hydrophobic and hydrophilic molecules and are suitable for photodynamic applications [3]. This work focuses on the development and optimization of complex liposomes for drug delivery based on the zwitterionic lipid 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), on the electrical negative lipids 1,2-dipalmitoyl-sn-glycero-3-phospho-(1′-rac-glycerol) (sodium salt) (DPPG) and 1,2-dioleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DOPG), and on cholesterol (CHOL), produced by sonication and extrusion methods. Lipid mixture was prepared with different composition in chloroform-methanol and liposomes were prepared by thin-film hydration method [4]. The suspensions were submitted to sonication or extrusion through a 200 nm polycarbonate membrane. Dynamic light scattering analysis was employed to compare size and polydispersity. Figure 1 shows the comparison between the two methods using 3 different lipid compositions namely, C1: DPPC+DPPG; C2: DPPC+DPPG+DOPG; C3: DPPC+DPPG+CHOL). While C2 and C3 liposomes produced by sonication show sizes around 150 nm, the ones prepared by extrusion present smaller sizes. However, C1 liposomes prepared through sonication present higher sizes (more than 1000 nm) while through extrusion C1 liposomes have diameter around 120 nm. Another major difference between the methods was the polydispersity indexes, above 0.3 and below 0.2 for sonication and extrusion, respectively. Therefore, sonication method produced small liposomes with DPPC and DPPG in presence of cholesterol or DOPG, but all the formulations present a moderate polydispersity index, which results in non-homogeneous liposomes size distribution. Extrusion through a 200 nm membrane enables the downsizing of all liposomes formulations, achieving a more homogeneous population of particles, which makes extrusion the selected method for further studies with the encapsulation of photosensitizer molecules in liposomes.

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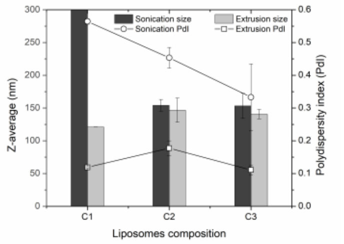

Figure 1: Comparison of size and polydispersity index (PdI) for different liposomes compositions produced through extrusion and sonication methods.

A Circular Model for Electron Configurations in 2D Heterostructures at High Magnetic Field

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The principles of self-organization of one-component charged particles, confined in circular external potentials are discussed by means of a circular model (CM) approach. We focus on the pinned quantum electron configurations localized in 2d heterostructures by intense magnetic fields. In the CM we derive a system of equations which allows us to determine equilibrium configurations for an arbitrary, but finite, number of charged point particles distributed over several rings. Our approach reduces significantly the computational effort in minimizing the energy of equilibrium configurations and demonstrates a remarkable agreement with the values provided by molecular dynamics (MD) calculations. The predictions of our model may in fact be used to feed other methods with sensible initial configurations to help minimize computational effort. With the increase of particle number, we find a steady formation of a centered hexagonal lattice that smoothly transforms to valence circular rings in the ground-state configurations. Although we address the classical limit of a quantum system, our approach could also shed light on the nature of self-organization of colloidal particles in organic solvents, charged nanoparticles absorbed at oil-water interfaces, electrons trapped on the surface of liquid helium or ionized plasmas.

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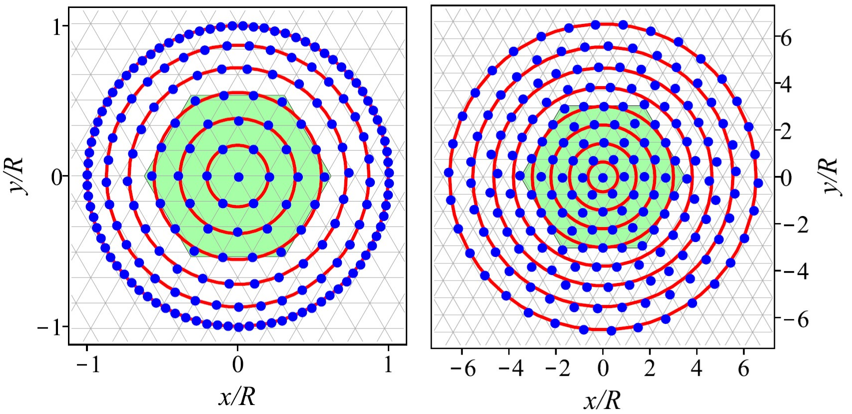

Figure 1: Examples comparing the CM (rings) and the MD results (dots) for $n = 187$ particles confined in disk (left) or harmonic (right) potentials. The *core* (green) region with {**1**,**6**,**12**,**18**,**24**} particles exhibits a clear hexagonal pattern. The external *valence* shells show an almost perfect circular structure.

Glucose Oxidase Enzyme Immobilized on a Nanostructured Pencil Graphite Electrode for Biosensor and Biofuel Cell Applications

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The use of ubiquitous and inexpensive materials in electrode construction is an established trend in the modern electrochemistry. For instance, paper-based materials and pencil graphite are examples of electrodes commonly used for sensing applications. Pencil graphite electrodes (PGE) can be a viable alternative to more conventional and expensive electrodes such as platinum and glassy carbon due to their negligible cost, availability, presenting also good electrical conductance properties. These advantages are more evident when disposable applications are equated. Moreover, a wide variety of sizes are commercially available enabling miniaturization of the active site and the whole PGE. Nanostructuration of PGEs can always compensate some lack of performance. Carbon-based nanomaterials not only serve as electron transfer enhancers between the electrode and analyte in solution but also they can serve as bridge or substrate for attachment of biological entities (such as enzymes) to facilitate direct electron transfer (DET). The immobilization of biological entities in these inexpensive electrodes can therefore produce miniaturized, cheap and disposable biosensors or biofuel cells. Particularly, the immobilization of glucose oxidase (GOx) for fabrication of glucose biosensors is important for the clinical field but can also be valuable for monitoring certain contaminants through an inhibitory detection principle [1]. The objective of the present work is the development and characterization of a pencil graphite bioelectrode comprising immobilized glucose oxidase (GOx) capable of achieving DET. The electrical wiring between GOx and the electrode is accomplished by using a tethering agent that binds to the enzyme via covalent amide bonds and adheres to the nanotube walls through irreversible π-π stacking with the aromatic group [2]. First, a 2 mm diameter PGE was mechanically polished, rinsed with water and further modified with single-walled carbon nanotubes (SWCNT) by dropcast and left to dry. Then the modified PGE was immersed for 2 h in a pyrene-based compound and rinsed with water. Finally, PGE was incubated overnight in GOx solution (10 mg mL^{-1}) and rinsed with water before analysis. Redox peaks obtained by cyclic voltammetry with the PGE-SWCNT-GOx biosensor in the absence of glucose proved the DET feature. Detection of glucose was performed by amperometry showing a sensitivity of about 29 µA mM^{-1} cm^{-2} and a limit of detection of 27 µM. The affinity of the bioelectrode towards glucose makes it appropriate to be used as a biosensor or a biofuel cell.

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