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Under the same roof will be held 4 International Conferences (graphIn, NanoSpain, IC2 and 3PM), a vast exhibition showcasing cutting-edge advances in nanotechnology research and development, an industrial forum and a brokerage event (one-to-one meetings).

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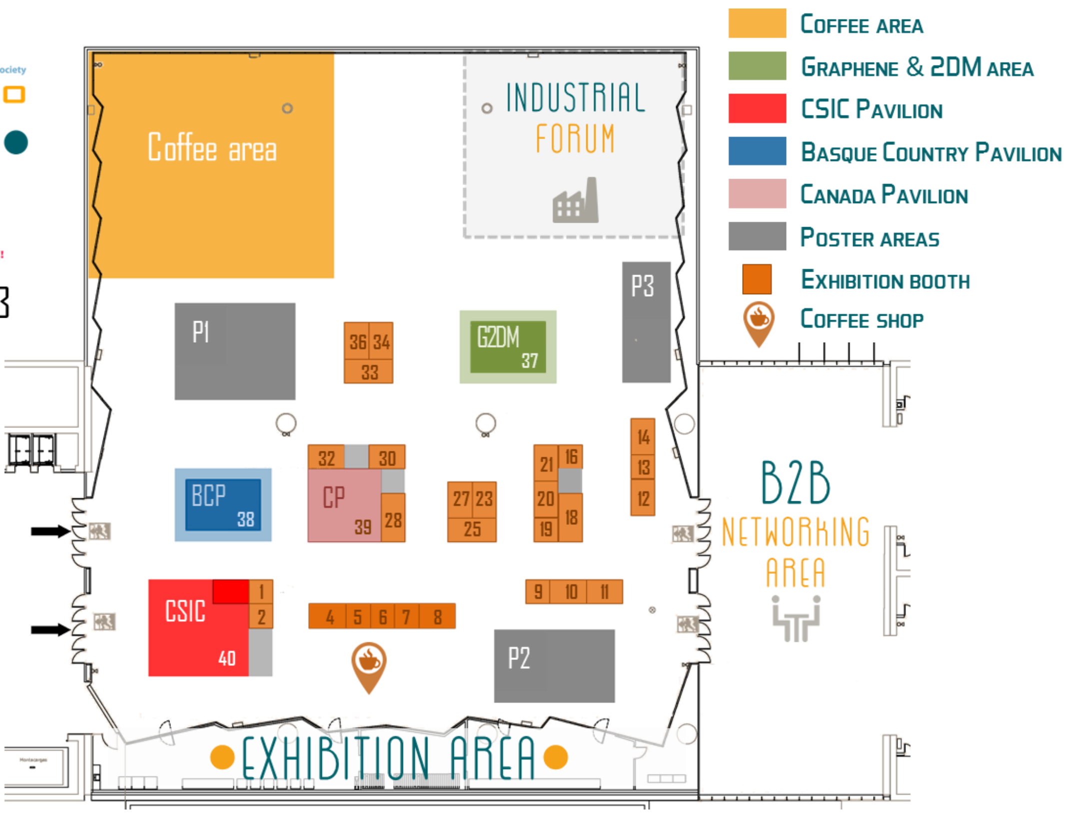

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PLENARY

Nanopores such as molecular sieves, catalysts and containers

Avelino Corma Canós

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It is possible to prepare crystalline nanoporous materials with high thermal and hydrothermal stability, with frameworks formed by SiO_2 or SiO_2-Al_2O_3 tetrahedras. It is possible to prepare the nanomaterial with pores within the size of different molecules and in this way they can act as molecular sieves. We will show by controlling pore dimension and framework vibration it is possible to separate gas molecules with differences in dimensions lower than 0.02nm. We will also show how to introduce into the pores in a one pot synthesis metals ranging from single atoms to nanoclusters and nanoparticles.
Finally we will present how the reactivity of metal or other active sites introduced within the pores can act, simultaneously, for molecular separation and catalytic transformations.

"Surface Attophysics"

Pedro Miguel Echenique

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Femtosecond and subfemtosecond time scales typically rule electron dynamics at surfaces. I will analyze briefly electron dynamics at surfaces and nanostructures with emphasis on surface attophysics, namely streaking experiments. Intra atomic delays and propagation effects will be analyzed.

References

"Intra-atomic Delays in Attosecond Time-resolved Solid State Photoemission"

F. Siek, S. Neb, P. Bartz, M. Hensen, Ch. Strüber, S. Fiechter, M. Torrent-Sucarrat, V. M. Silkin, E. E. Krasovskii, N. M. Kabachnik, S. Fritzsche, R. Díez Muiño, P. M. Echenique, A. K. Kazansky, N. Müller, **W. Pfeiffer**, U. Heinzmann

Science, 357, 1274 (2017)

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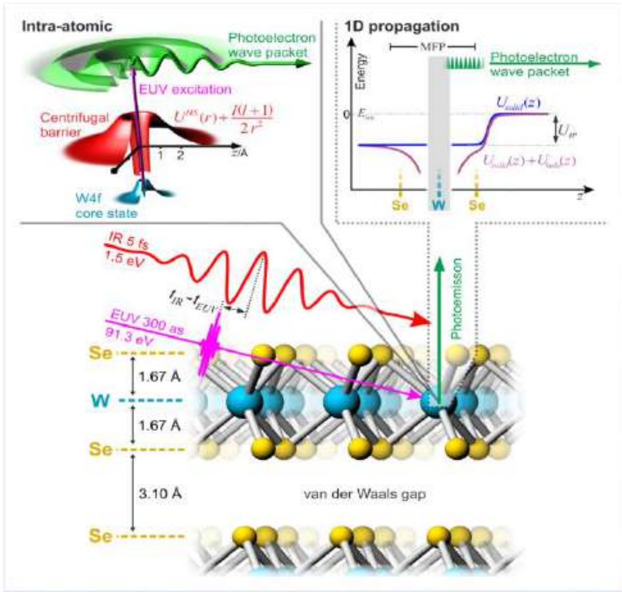

NANOSPAIN2018 – SPEAKERS

Transport in and into graphene: Insights from transport calculations

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Devices based on stacked van der Waals heterostructures of two-dimensional (2D) materials are promising candidates for future atomically thin, flexible electronics. A key advantage is precise control of the carrier density by a gate. Atomistic first principles transport calculations, which can take voltage biases, currents, and gate potentials into account, can yield important insights into the behaviour of the novel device architectures and phenomena based on the 2D materials.
I will in the talk illustrate this point by presenting examples of transport calculations based on Density Functional Theory combined with non-equilibrium Green's functions (DFT-NEGF) [1], or the Boltzmann equation [2].

The examples include the role of the gate potential for the contact resistance between 2D materials, and how it depends on the stacking order and gate position (see Fig. 1)[3], gate-induced flexural electron-phonon scattering mechanism in graphene[4], the critical role of phonon-scattering in point-contacts to graphene[5], and finally, the dependence of contact resistance on the metal used for contacting graphene edges[6]

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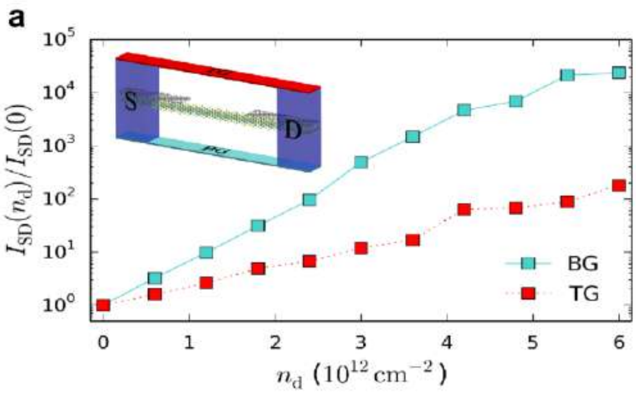

Figure 1: Source-drain current as a function of gate-induced carriers in a graphene-contacted MoS2 channel for gate at top or bottom (insert). From Ref. [3].

A bottom-up view at the aggregation of a bacterial functional amyloid protein

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Biofilms are groups of microbial cells that are encased in an extracellular matrix (ECM) composed mainly of proteins and polysaccharides. Biofilms can be beneficial, for example when protecting the roots of plants, but they are often detrimental to the host: their formation on medical devices and implants such as catheters, artificial hips, or contact lenses may lead to both acute and chronic infections. The ECM functions as inter-cellular glue and it is also known to protect the cells from external toxins. The major proteinaceous component of the ECM forms fibrillar appendages that are 'functional amyloids'. In contrast to amyloid proteins that are related with disease, functional amyloids are not considered harmful but rather, they have a functional role as they provide mechanical stability to biofilms. The formation of amyloid fibers has been extensively studied in the context of neurodegenerative diseases such as Alzheimer's and Parkinson's disease. However, **very little is known about the mechanisms of functional - amyloid - fiber formation**. In my lab, we use the soil bacterium *B. subtilis* as a model organism for biofilm formation. Specifically, we study inter- and intra- molecular processes that lead to aggregation of the functional amyloid TasA in solution and in the presence of membranes. Our study combines Biochemical methods, spectroscopy (CD and FTIR) as well as Atomic Force Microscopy (AFM) to measure and quantify actual protein – protein interactions. Understanding the properties of the ECM and the mechanisms that underlie its assembly may lead the way for antibiofilm drugs that target the extracellular matrix.

Figures

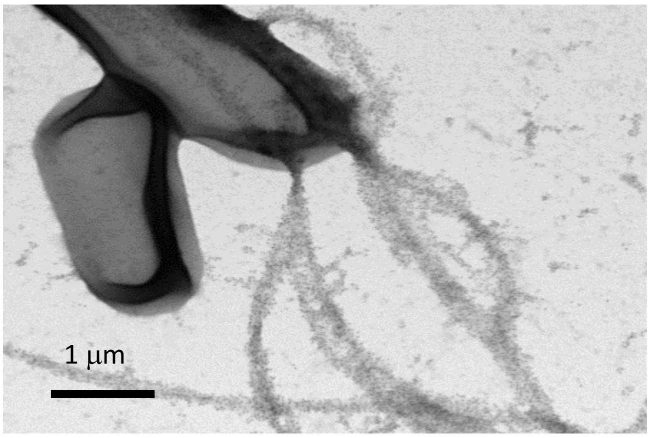

Figure 1: Transmission Electron Micrograph (TEM) view of single *Bacillus subtilis* cells showing the TasA fibers emerging from their surface.

Nanoscale Chemical and Electronic Mapping of Carboxyl Graphene Oxide using TERS

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In recent years, Tip Enhanced Raman Scattering (TERS) imaging made a dramatic progress from "once in a lifetime experience" to a routine everyday characterization tool for nanoscale Raman imaging of various materials. This progress was mainly determined by the advent of new generation of TERS instrumentation, development of advanced TERS imaging modes and availability of highly reproducible commercially available TERS probes with high enhancement factors.

Since TERS is intrinsically a hyperspectral imaging tool, it does not rely on apriori knowledge of the spectral properties of the investigated materials and therefore allows discovery of unexpected Raman peaks and mapping the distribution of their intensities. Cross-correlating the nano-Raman maps with other channels provides by scanning probe microscopy such as the topography, surface potential, conductivity, photocurrent, friction etc, is another powerful tool allowing comprehensive characterization of novel materials at nanoscale.

We'll illustrate usefulness of TERS imaging and cross-correlation of nano-Raman with other SPM channels by probing the distribution of structural defects and chemical groups on a graphene oxide surface. We demonstrate mapping of chemical groups on carboxyl graphene oxide (GO-COOH) surface with an unprecedented spatial resolution of ≈ 10 nm using TERS.

Furthermore, we extend the capability of TERS by in-situ measurement of local electronic properties in addition to the topography and chemical composition at the sample surface. In-situ topographical, electronic and chemical nanoscopy of the GO-COOH surface reveals that the Fermi level on GO-COOH surface increases with increasing ID/IG ratio, enabling correlation of the local defect density to Fermi level at nanometre length-scales for the first time.

Figures

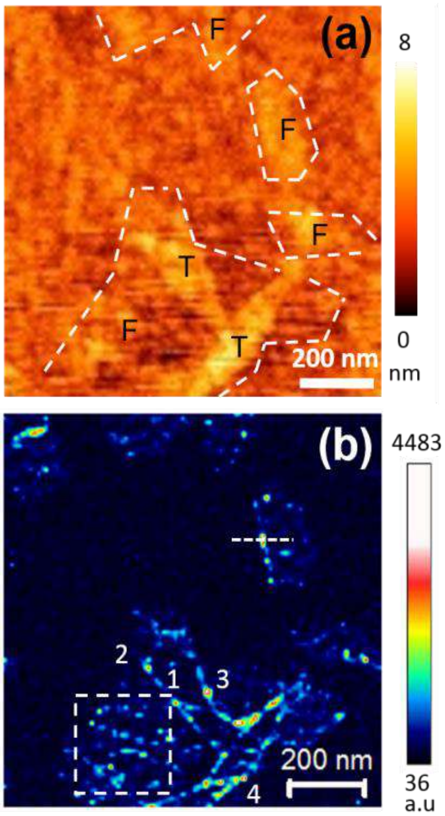

Figure 1: (a) AFM image and (b) high-resolution TERS map of different graphene oxide flakes. The optical resolution is ~ 10 nm.

Electronic and optical properties of strained graphene and borophene

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When passing an optical medium in the presence of a magnetic field, the polarization of light can be rotated either when reflected at the surface (Kerr effect) or when transmitted through the material (Faraday rotation). This phenomenon is known as a direct consequence of the optical Hall effect arising from the light-charge carrier interaction in solid state systems subjected to an external magnetic field, in analogy with the conventional Hall effect. The optical Hall effect has been explored in many thin films and also more recently in 2D materials. Here, an alternative approach based on strain engineering is proposed to achieve an optical Hall conductivity in graphene without magnetic field [1]. Indeed, strain induces lattice symmetry breaking and hence can result in a finite optical Hall conductivity. First-principles calculations also predict this strain-induced optical Hall effect in other 2D materials. Combining with the possibility of tuning the light energy and polarization, the strain amplitude and direction, and the nature of the optical medium, large ranges of positive and negative optical Hall conductivities are predicted, thus opening the way to use these atomistic thin materials in novel specific opto-electro-mechanical devices.

Borophene, a recently synthesized two-dimensional monolayer of boron atoms, is expected to exhibit anisotropic metallic character with relatively high electronic velocities [2]. At the same time, very low optical conductivities in the infrared-visible light region have been reported. Based on its promising electronic transport properties and *a priori* high transparency, borophene could become a genuine LEGO piece in the 2D materials assembling game. Such early suggested properties demand for an in depth investigation of borophene electronic structure. Moreover, borophene is naturally degraded in ambient conditions and it is therefore important to assess the mechanisms and the effects of oxidation on borophene layers. Optical and electronic properties of pristine and oxidized borophene have been investigated using first-principles techniques [3]. Optical response of the oxidized layer is found to be strongly modified suggesting that optical measurements can serve as an efficient probe for borophene surface contamination.

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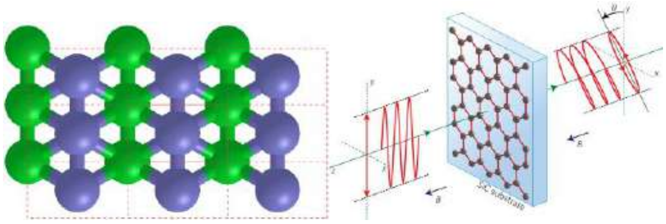

Figure 1: Electronic and optical properties of borophene and strained graphene

Nanotools to understand why proteins and nanoparticles induce an immune response

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Abstract

Immunogenicity (i.e. the ability of a particular substance to provoke an immune response in humans or animals) represents a major challenge for the development of new biotherapeutics (Figure 1). It is essential to predict what induces such an immune response which sometimes may lead to autoimmune diseases. Nanotechnology plays an increasingly important role in predicting the immunogenicity. In the past few years, we have developed spectroscopic and imaging techniques to identify the features that make proteins of our bodies immunogenic. We have previously characterized the interaction of the blood protein platelet factor 4 (PF4) with heparin (anticoagulant) and other polyanions[1]. By circular dichroism spectroscopy we have found that an increase in antiparallel β-sheet content of PF4 above 30% is associated with binding of anti-PF4/heparin antibodies (or immunogenicity)[2]. We have also shown using isothermal titration calorimetry that ~11 monosaccharides are required to drive the structural changes in PF4 leading to immunogenicity [3]. Additionally, we have shown by single molecule force spectroscopy that at least three polyanion bonds have to be formed to each PF4 molecule to induce a conformation to which the antibodies bind [3]. In addition, by engineering hybrid micro/nano-arrays we have investigated the interaction of antibodies with complex antigens and have monitored the behavior of immune cells[4]. Our work has been extended to other blood or non-blood, soluble or transmembrane proteins possessing mutations or post-translational modifications.

Currently, we investigate immunogenicity of nanoparticles which are known to stimulate and/or to suppress the immune response by binding to blood proteins. Although the compatibility of the nanoparticles with the immune system is largely determined by their physico-chemical properties (*e.g.* size, shape, charge, surface groups), the effect of nanoparticle properties on the immune system is little explored. We study how nanoparticles may become immunogenic.

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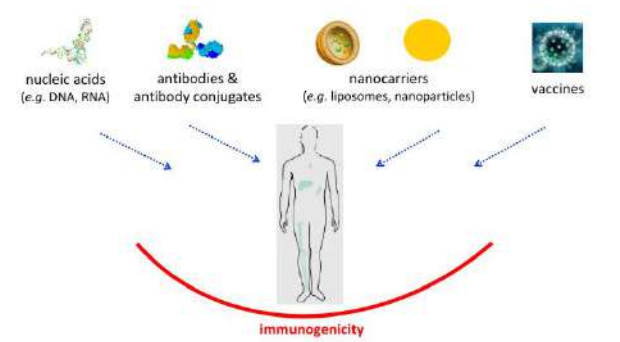

Figure 1: Schematic of nanobiotherapeutics which may induce immunogenicity.

Van der Waals spintronics with magnetic 2D crystals

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Abstract

It has been recently discovery that layered ferromagnetic compound, such as CrI_3, can be delaminated into 2D crystals that retain magnetic order down to the monolayer limit. This opens the venue both for interesting fundamental research [1] in quantum materials and exploration of new applications. In this talk I will present two types of Van der Waals device architecture that combine magnetic and non-magnetic 2D crystals. First, I will discuss the origin of the very large magnetoresistance observed in a tunnel junction with a spin-filter ferromagnetic barrier and graphite electrodes [2]. Second, I will propose a new in-plane spin valve where a graphene bilayer is sandwiched between two insulating ferromagnets[3]. Using both model Hamiltonians and DFT calculations we find that, when their spin orientation is antiparallel, a gap opens up at the Dirac point of the graphene bilayer.

Figures

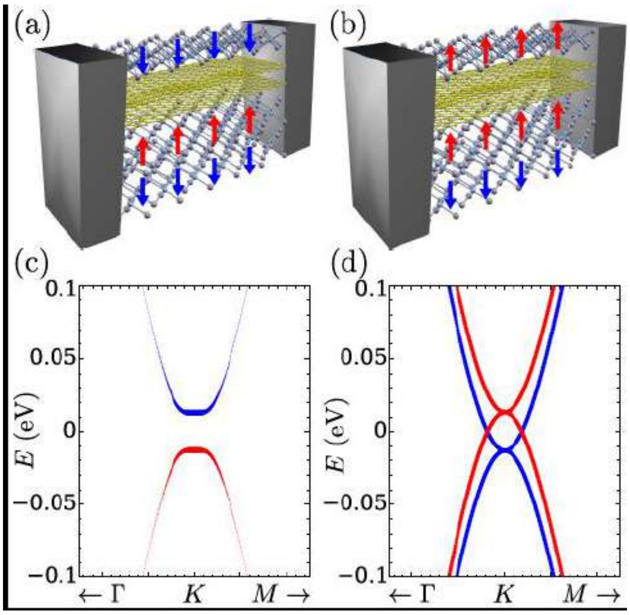

Figure 1: Scheme for current in plane graphene bilayer spin valve (See reference 3). A band-gap opens in the graphene bilayer when the spin orientation of the magnetic layers is antiparallel

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Novel Electronic States in Graphene Nanostructures

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A precise control and understanding of conformational or chemistry related electronic signatures in graphene nanostructures is crucial for their use in electronic and optoelectronic applications. In this talk, I will present some studies of electronic properties of graphene nano-structures that we have performed in collaboration with our experimental colleagues. Different aspects, such as the influence of the conformation or the effect of chemical doping, have been addressed.[1,2]

In particular, we have investigated the emergence of novel electronic states in carbon-based macromolecules and graphene nanoribbons. Our studies show that such peculiar states have similar origin as the image states of graphene, which exist in the vacuum region above and below the graphene layer.[3] Image states do not follow the atomic lattice modulation and behave as nearly-free electrons (NFE). When graphene is rolled into nanotubes or fullerenes, these states overlap giving rise to the emergence of 1D NFE bands or 0D Super-Atom Molecular Orbitals (SAMOs)[4].

Interestingly, we find that for graphene nanostructures there exist image states related to the 1D edge of graphene. Through the combination of scanning tunneling microscopy (STM) and density functional theory (DFT), we reveal the existence of a 0D-SAMO resonance in the central empty region of a planar carbon-based macromolecule.[5] Moreover, based on DFT calculations, we predict the emergence of 1D-NFE states in graphene nanoribbons, and we propose a way to confine them by modulating the width of the ribbons periodically, thus effectively creating 0D Super Atom States.

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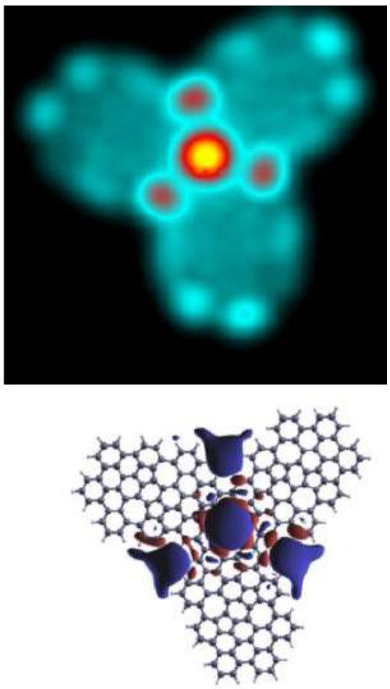

Figure 1: Electronic state with large weight in the pore region of the carbon based macromolecule. Upper panel: constant height dI/dV map. Lower panel: DFT wavefunction amplitude isosurface.

High spatial resolution mapping of catalytic reactions on single nanoparticles

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The critical role of low-coordinated metal atoms in surface reactions and heterogeneous catalysis has been firmly established. But despite the growing availability of tools enabling detailed in situ characterization, it has so far not been possible to directly probe the influence of various surface sites on the reactivity of single nanoparticles. Here we show that differently active regions within a given particle can be distinguished by mapping the chemical reactivity of N-Heterocyclic Carbene molecules (NHCs) attached to catalytic particles using synchrotron radiation-based infrared nanospectroscopy (SINS) [1]. It is demonstrated that compared to flat regions on top of the particles, the particles' periphery, containing low-coordinated metal atoms, is more active in catalysing oxidation, as well as reduction, of chemically active groups in surface-anchored NHCs. These results indicate that high spatial resolution vibrational spectroscopy measurements can correlate between surface properties and reactivity, uncovering differences in reactivity between neighbouring sites across the surface of single catalytic nanoparticles.

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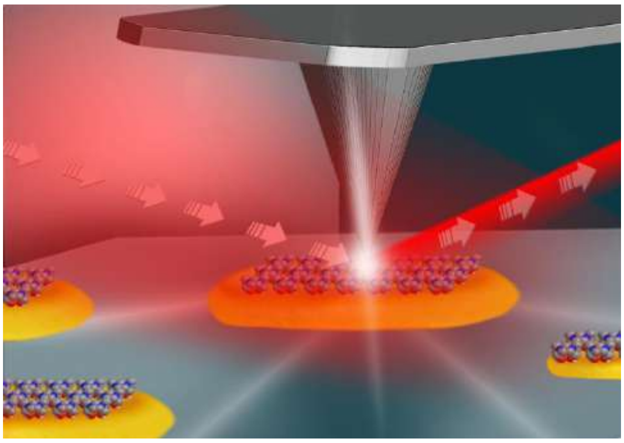

Figure 1: Schematic representation of the experimental approach. Chemical reactivity on the surface of single nanoparticles was measured by focusing a bright infrared beam into the apex of a thin tip with a diameter of 20 nm that monitored the chemical reactivity on the particle's surface.

Graphene and Beyond: Synthesis and Characterization of Atomic-Films

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The tremendous interest in 2D materials over the last decade is driven by their rich physics and device performance that hold great promise for future technological applications. The physical and chemical properties of these materials highly differ from their 3D counterpart. Therefore, the rational synthesis of atomic-films with the desired structure (number of layers, chemical composition, phase, etc.) is a critical prerequisite to fulfill the potential of materials.

In this talk, I will address the different approaches we have to grow atomic-thin materials and review recent advances in the growth and characterization of single- and few-layer van der Waals solids. I will focus on gas phase techniques, starting from graphene and hexagonal boron nitride (*h*-BN), throughout the transition metal dichalcogenides (TMDs) family and finalize with more exotic 2D materials. The similarities and differences between these materials and their respective growth mechanism will be discussed. For example, the growth of graphene and *h*-BN is considered to occur catalytically on transition metal surfaces [1,2, 3]. TMD growth, on the other hand, does not appear to be a catalytic process, therefore, opening the opportunity for their direct synthesis on arbitrary substrates [4]. The advantages and disadvantages of both growth-types will be elaborated. I will finalize by describing our attempts for the direct synthesis of 2D heterostructures and how they can be assembled into novel 3D structures.

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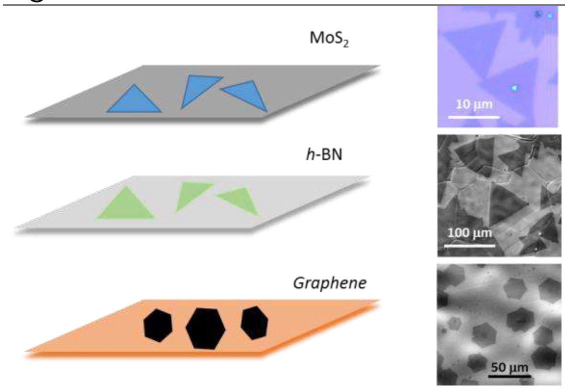

Figure 1: Chemical vapor deposition of different 2D materials.

Patent protection of nanomaterials and nanotechnology related inventions

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Nanomaterials and nanotechnology related patent applications are not examined differently from patent applications belonging to other fields: patent requirements must be fulfilled in order for the application to be granted.

Applicant has to specify in the claims what he understands to be "nano" in order to avoid clarity objections. Furthermore, prior art could become novelty destroying if a broad interpretation of the claim was made.

As selection inventions, nanomaterials and nanotechnology related inventions cannot merely rely on size. The simple fact of miniaturizing without the presence of an additional effect does not involve inventive step. However, if an invention provides a new technical advantage which was not found in the prior art and it was not obvious for a skilled in the art, the miniaturization could be considered inventive.

The highly sophisticated methods and tools for manipulating materials in the nanometre, or even molecular, range may go beyond the knowledge of the person of average skill in the field, therefore, the application as a whole must disclose the invention in such a way that a person skilled in the art can carry it out.

Examples of nanomaterials and nanotechnology related inventions will be carefully presented and discussed in view of patent requirements.

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Figures

Figure 1

Figure 2

Ab-initio simulations of metal clusters

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Our optimal implementation of time-dependent density functional theory within linear response allows computing the optical properties of systems with several thousands of atoms [1,2]. We applied this method to study the dependence of the near-field enhancement and localization on the structural details of the plasmonic nano-gaps [3,4], the different size dispersion of the plasmon resonance of silver and sodium nanoparticles and how this behaviour correlates with the presence of 4d electrons in the Ag case [2], and more recently to describe valence EELS [5].

In this talk I will concentrate mostly in the correlation between transport properties across sub-nanometric metallic gaps and the optical response of the system. In Ref. [6] we presented a study of the simultaneous evolution of the structure and the optical response of a plasmonic junction as the particles forming the cavity approach and retract. Atomic reorganizations are responsible for a large hysteresis of the plasmonic response of the system, which shows a jump-to-contact instability during the approach process and the formation of an atom-sized neck across the junction during retraction. Our calculations show that, due to the conductance quantization in metal nanocontacts, small reconfigurations play a crucial role in determining the optical response. We observe abrupt changes in the intensity and spectral position of the plasmon resonances, and find a one-to-one correspondence between these jumps and those of the quantized transport as the neck cross-section diminishes. These results point out to a connection between transport and optics at the atomic scale at the frontier of current optoelectronics.

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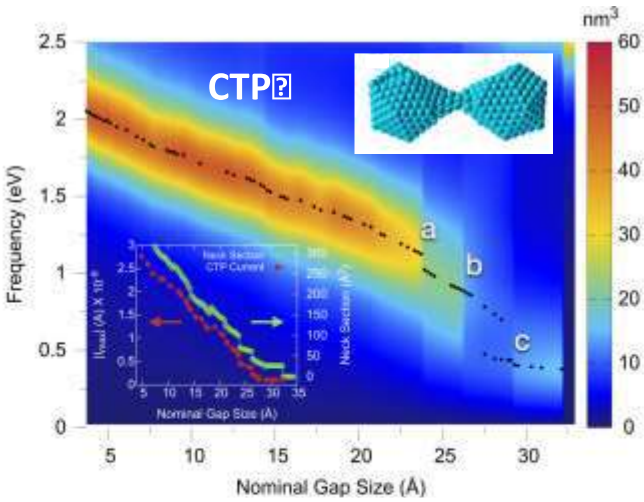

Figure 1: There is a one-to-one correspondence between the jumps in the current flowing through the metal neck, its cross-section and the far-field optical response at the frequency of the so-called charge transfer plasmon (CTP).

Elementary reactivity at the nanometer scale: the abstraction of atoms from metal surfaces.

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The rationalization of elementary reactivity at surfaces is of prime importance to numerous natural and technological areas. From a fundamental point of view, the way the energy concomitant to any chemical reaction is distributed among the desorbing molecules degrees-of-freedom and the surface is not entirely pictured. Over the last few years, we have been developing reaction dynamics simulations to investigate this issue for the recombination of H_2 and N_2 resulting from atomic adsorbate abstraction by atom scattering off the W(100) and W(110) covered surfaces. Potential energy surfaces, built from density functional (DFT) theory calculations, have been used to simulate, within the framework of classical dynamics (including semi-classical corrections), the subpicosecond Eley- Rideal and Hot-Atom processes. The implementation of effective models to account for energy dissipation to surface phonons and electron-hole pair excitations, have allowed to rationalize the non-adidabatic dynamics of atom abstraction at metal surfaces. Such dissipation significantly affects the length scale over which reactivity occurs. Some examples [1-3] of this ongoing research will be here shown.

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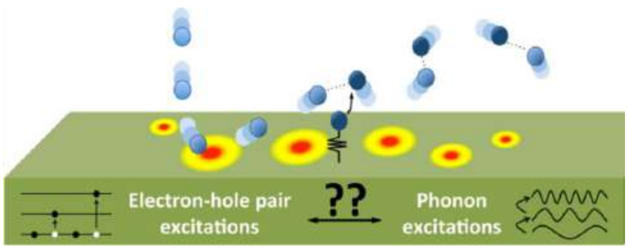

Figure 1: Dissipation channels upon atom abstraction from a metal surface

Elementary Phenomena in Hybrid Graphene Nanoribbons on Surfaces

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Abstract

Large aromatic carbon nanostructures are cornerstone materials due to their increasingly role in functional devices. Chemical routes have been established allowing us to steer synthesis by properly selecting the shape of organic precursors and produce large molecular platforms with tunable intrinsic properties such as the electronic band-gap, its magnetic behaviour, or its reactivity. In this presentation, I will summarize results regarding the production of graphene nanoribbons and other carbon nanostructures with interesting electronic phenomenology. We combine high resolution STM imaging with local spectroscopy to explore the effect of precursor shape and composition in electronic functionality of the ribbons. I will show that narrow chiral (3,1) graphene nanoribbons (cGNRs) behave as one-dimensional semiconductors[1]. Doping of nanoribbons can be introduced by functional group edge modifications[2]. For example, amino groups attached to cGNRs (Figure 1) induce a characteristic shift in the energy of both conduction and valence band. I will also show the width dependence of band structures of cGNRs. Wider cGNRs are metallic and exhibit localized edge states. Finally, I will show that it is possible to incorporate magnetic molecular species bound to a ribbon (Figure 2). We show that the molecular spin survives in the ribbon by using spin-excitation inelastic spectroscopy[3].

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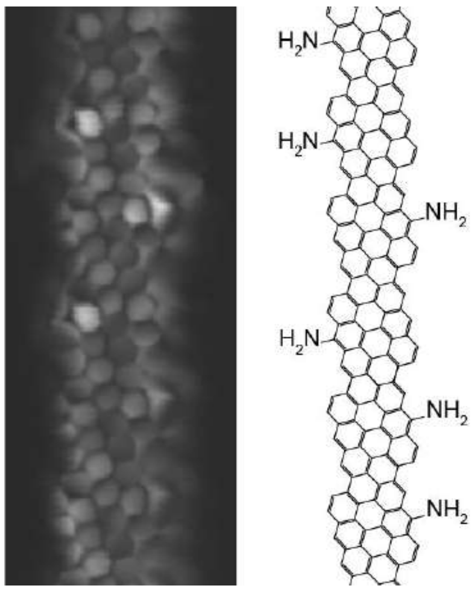

Figure 1: Chiral (3,1) graphene nanoribbons functionalized with amino groups.

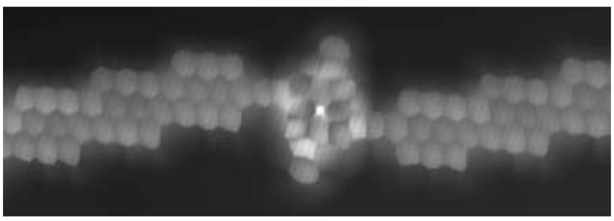

Figure 2: Fusing magnetic porphyrine into chiral (3,1) graphene nanoribbons.

CHALLENGES IN POLYMER NANOTECHNOLOGY APPLICATIONS: PATTERNING STRATEGIES AND POLYMER COFINEMENT EFFECTS

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Abstract

Most recent challenges of nanotechnology demand the combination of specific chemical functionalities and the easy, high-throughput manufacturing of nanoscale elements over large distances. Because of their easy tunability of their properties via chemistry and the fact that they can be readily nanostructured over large scales, **polymers** are becoming, with no doubt, one of the most versatile materials available for nanotechnology. Good examples of the above are polymer nanostructures processed from anodic aluminum oxide (AAO) templates (Figure1a)[1].
In this work, we report an overview of some of the most recently developed experimental procedures to obtain polymer nanostructures using nanoporous AAO: i) Core-shell polymer-polymer nanostructures by the combination of double infiltration process, (Figure1b)[1]; ii) Core-shell metallic-polymer nanostructures by the combination of electrochemical and chemical routes; iii) dual sized polymer nanostructures[2], and iv) micropatterned surfaces[3]. Finally, we will also highlight how confinement effects influence the fabrication of a polymer nanostructure in-situ synthesized in AAO "nanoreactor" (Figure 1c)[4] and the polymer properties (crystalllization, dynamics, etc)[5]

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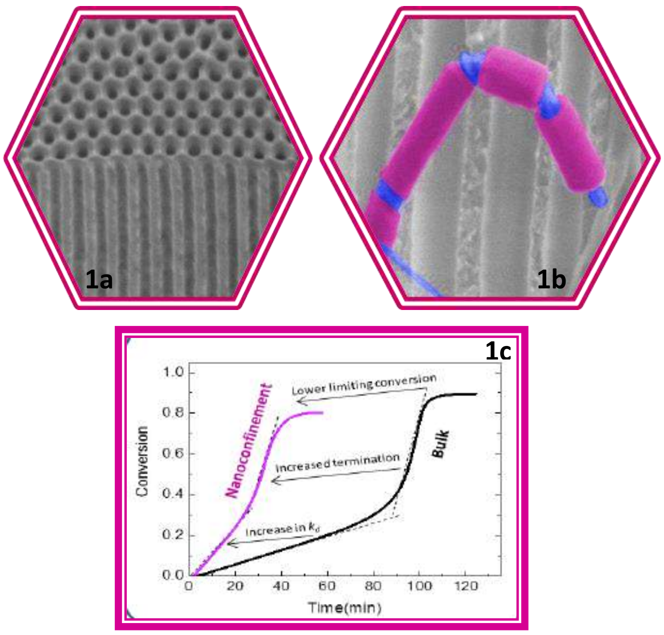

Figure 1: SEM images: Cross section of AAO template (a), PCL-PS core-shell nanostructure (b); Polymerization kinetics in confinement (c)

Emergent Spin-Orbit Related Phenomena in Intercalated Graphene

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Graphene is a material that has a negligible Spin-Orbit Coupling (SOC) in its pristine state. However, the intercalation of adequate metals (e.g. Pb underneath gr/Ir(111)) can transfer to graphene a giant SOC [1] of the order of 80 meV, as demonstrated by first principle calculations, STM and spin-resolved ARPES [2].

Graphene can be intercalated with ferromagnetic metals (e.g. Cobalt) becoming n-doped and with an intense electrical field at the gr/Co interface. This, rather unexpectedly, originates a giant chiral Dzyaloshinskii Moriya Interaction (DMI) at the gr/Co interface that, in addition to the SOC-induced DMI at the Co/Pt interface, creates in a chiral spin texture in gr/Co(111)/Pt(111) layered heterostructures grown epitaxially on MgO(100) [3]. The discovery of a strong DMI at the Graphene/Cobalt interface is a crucial step to promote 2D materials spin-orbitronics based on the electrical control of the transport and manipulation of topologically protected magnetic structures, such as chiral domain walls and skyrmions.

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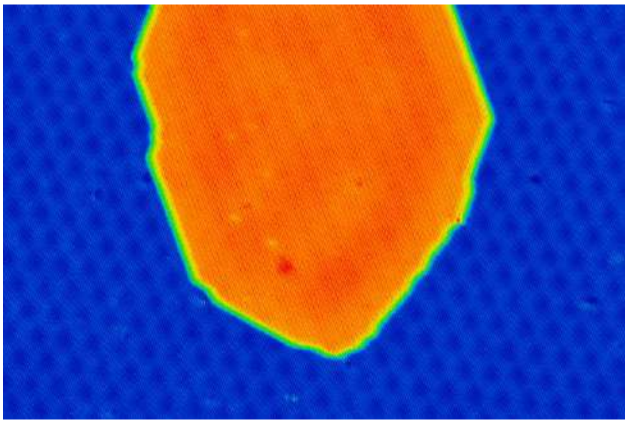

Figure 1: STM image of graphene/Ir(111) with a monolayer of Pb intercalated below graphene.

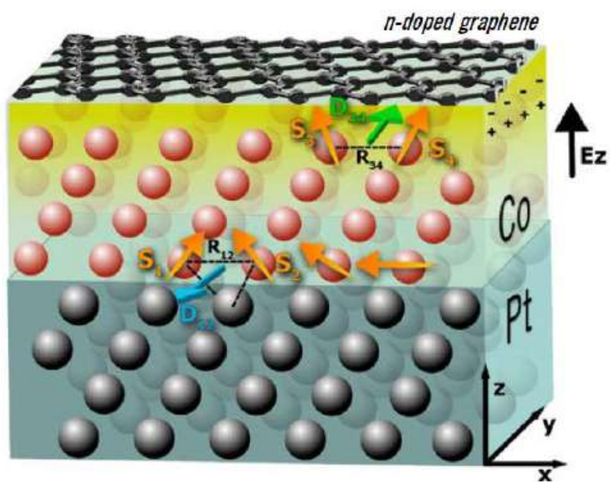

Figure 2: Sketch of the interplay between Spin-Orbit Coupling-induced Dzyaloshinskii Moriya Interaction (DMI) at the Co/Pt and opposite Rashba-type DMI at the gr/Co interfaces.

Layered and 2D materials: electronic properties and structural instabilities from first principles

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I will present some of our recent work [1-3] on the understanding of the electronic properties of layered materials and their 2D relatives by means of first principles electronic structure calculations. In particular, I will focus on the correlation between the crystal structure and the electronic properties, with special emphasis on the structural instabilities with an electronic origin. This will be done in connection with recent experimental studies that have been able to demonstrate the presence of charge density waves (CDW) in several 2D single-layer materials like $NbSe_2$ and $TiSe_2$. The evolution of the CDW with external electrostatic doping, which has been achieved experimentally using field effect transistor setups, will be analysed for the case of $TiSe_2$ [4].

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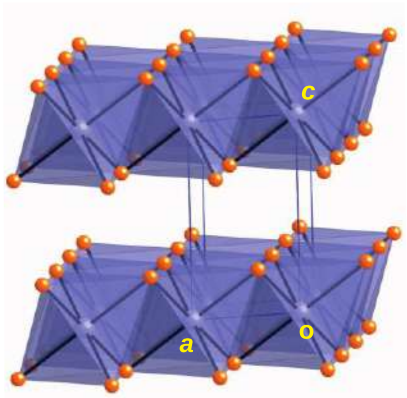
(a)



(b)

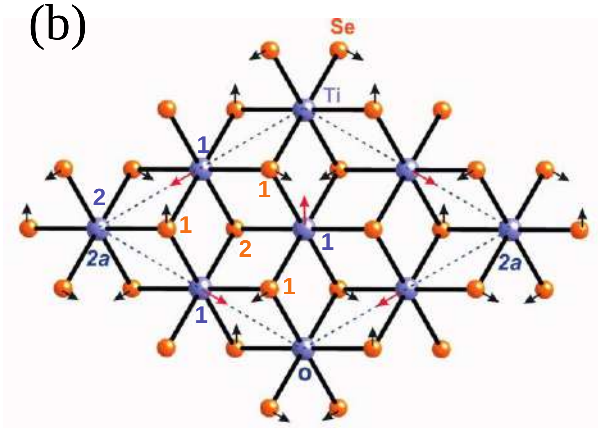


Figure 1: (a) Crystal structure of $TiSe_2$. (b) Schematic representation of the displacements occurring in a single-layer of the 2x2 CDW structure of $TiSe_2$.

Sustainable carbon: graphene water, nanotube water and eco friendly conducting rubbers, electrocatalysts and supercapacitors

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(i) Full exfoliation of graphite to form thermodynamically stable, negatively charged, graphene (graphenide) flakes in solution can be achieved by dissolution of graphite intercalation compounds (GICs) in low boiling point aprotic organic solvents under inert atmosphere.[1] Graphenide can be transferred to *degassed* water as single layer graphene. The organic solvent can then be evaporated to remain with an aqueous graphene suspension of ca 400 m^2/L concentration under ambient atmosphere. The Raman spectra (2.33 eV laser) collected in situ on such dispersions show typical signals of single layer graphene.[2-5]
(ii) Food waste can be transformed into graphitic carbon and renewable hydrogen using an innovative low energy microwave plasma process at industrial scale. The obtained nanocarbon is obtained through energy efficient transformation of methane resulting from decomposition of food waste.[6] After purification, well defined, high concentration aqueous dispersions of nanocarbons are obtained and characterized. They contain calibrated multilayer graphene particles. Conducting inks, films, rubbers and supercapacitors can be prepared from these dispersions.[7,8] Additionally electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) made of Fe nanoparticules / nanocarbon composite have been prepared with these multilayer graphenic particles.[9]

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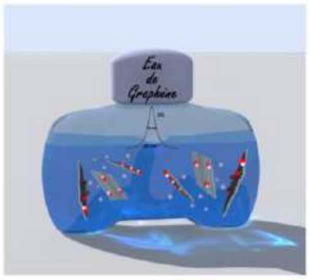

Figure 1: a scheme of graphene layers stabilized by OH- adsorption

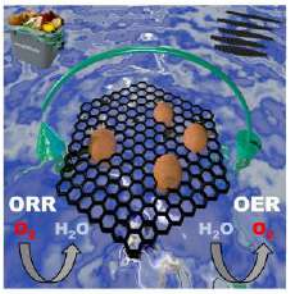

Figure 2: A scheme of nanographene / nanoparticle constituting an efficient electrocatalyst.

Novel DNA-Based Molecules and Their Charge Transport Properties

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Abstract

The DNA double-strand recognition, as well as the ability to manipulate its structure open a multitude of ways to make it useful for molecular electronics. Step by step we improve the synthesized constructs and the measurement methods of single DNA-based molecules. I will present new DNA-based molecules and report on our measurements of their properties. I will also present new and surprising results on dsDNA molecules.

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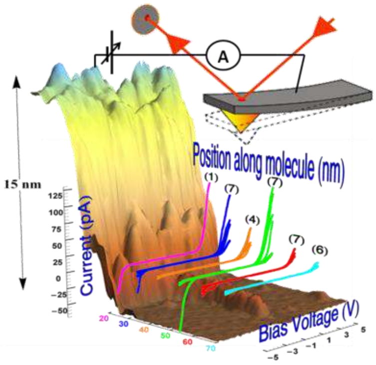

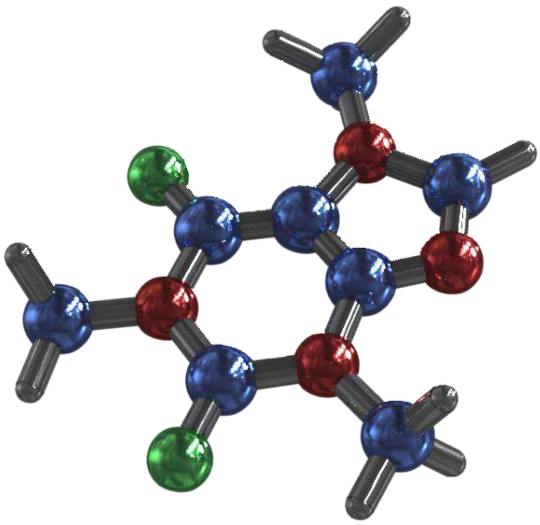

Figure 2: Insert caption to place caption below figure (Century Gothic 109

CeO_2 nanoparticles as safe CT X-ray contrast imaging agents

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Use of X-ray computed tomography (CT) has increased dramatically over the last years in many countries owing to its availability, low cost and high resolution. An estimated 82 million scans were performed in the U.S. in 2016. However, a main concern about CT scans is the exposure to ionizing radiation. One study estimated that as many as 0.4% of current cancers in the U.S. are due to CTs performed in the past. Thus, an important issue is how to reduce the radiation dose during CT examinations without compromising the image quality. Contrast agents are regularly administered in order to improve image contrast. High Z-based nanoparticles have gained attention lately because they show notable advantages over commercial iodine-based compounds. For instance, they allow longer circulation times and deliver a large amount of heavy atoms[1]. In this work we present CeO_2 NPs as potential CT contrast agents. Cerium possesses high atomic number and electron density, it is biocompatible and CeO_2 NPs show antioxidant and anti-inflammatory properties, providing radioprotective capabilities [2]. In addition, given that the contrast enhancement depends both on the tube potential (kVp) and energy spectrum, Au-CeO_2 hybrides have also been prepared, increasing thus X-ray energy absorption range.

Firstly, it has been assessed the stability of the colloidal samples at the high concentrations required by the CT instruments (>100 mM), which are prone to aggregation and precipitation. In vitro CT results (Figure 1) indicate that, at equal molar concentrations, Ce-based NPs produce higher X-ray contrast than iodine. Additionally, we have observed that CeO_2 and Au-CeO_2 NPs act as a free-radical scavenger (Figure 2), reducing thus the radiation adverse effects of using metals in CT imaging [3].

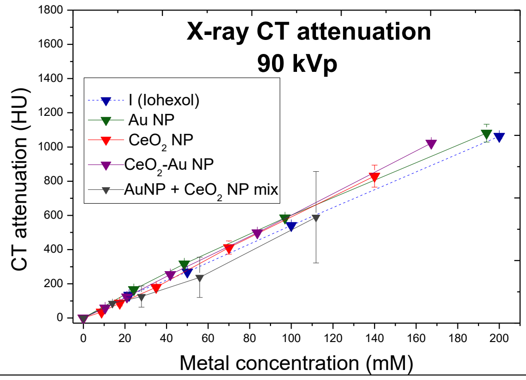

Figure 1: CT contrast (HU) as function of the metal concentration (mM).

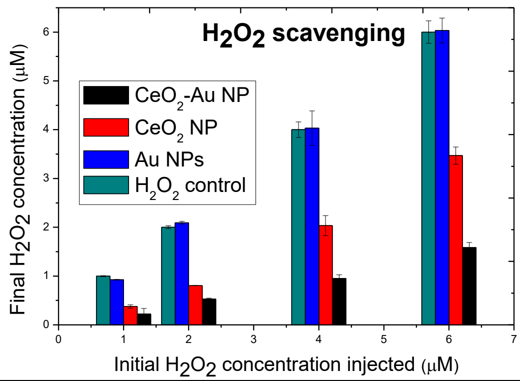

Figure 2: H_2O_2 scavenging tested with Amplex Red Assay

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2D materials for Spin and Valleytronics: Theoretical Perspective

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Abstract

The physics of graphene can be strongly enriched and manipulated by harvesting the large amount of possibilities of proximity effects with magnetic insulators, strong SOC materials (transition metal dichalcogenides-TMDC, topological insulators, etc). Simultaneously, the presence of extra quantum degrees of freedom (sublattice pseudospin, valley isospin) points towards new directions for information processing [1,2], extending the playground to valleytronics, multifunctional electronic devices or even disruptive quantum computing by harnessing all these degrees of freedom in combination with electromagnetic fields or other external fields (strain, chemical functionalization, etc) [3,4].

In this talk, we will present the foundations of spin transport for Dirac fermions propagating in supported graphene devices or interfaced with strong SOC materials. The role of "valley and sublattice pseudospins" in tailoring the spin dephasing and relaxation mechanisms will be explained as well as the impact of strong SOC proximity effects on spin lifetime anisotropy, weak antilocalization and SHE, in the context of recent experiments [4-6].

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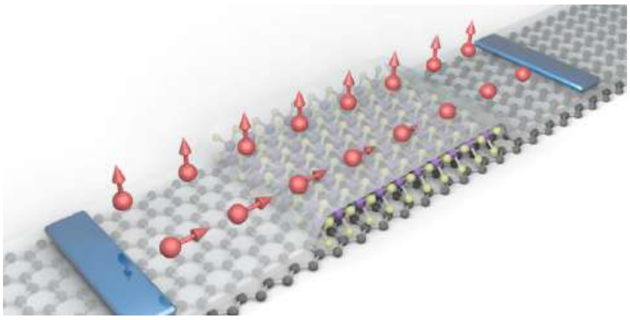

Figure 1: Schematic of spin transport tuning by proximity effect in graphene/TMDC heterostructures

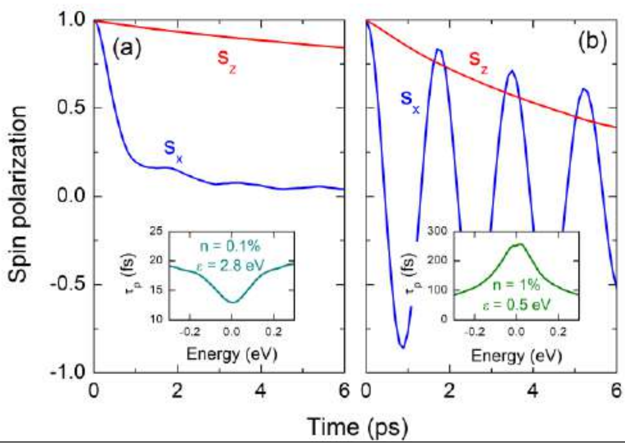

Figure 2: Time dependent spin evolution of wavepackets initially injected with in-plane (Sx) or out-of-plane (Sz) polarization, and for strong (a) or weak (d) electron-hole puddles disorder

Nanomaterials for Energy Storage

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The trends in energy consumption and production are changing toward a more sustainable model. Within this new framework, the development of improved energy storage systems is essential for the consolidation of different renewable energy sources as well as to give response to the increasing number of portable electronic devices, starting from consumer electronics and reaching the hybrid electric vehicle (HEV).

In this change of energy paradigm, the role of energy storage systems is crucial. Batteries and supercapacitors are the most efficient electrochemical energy storage technology currently available. The design and development of advanced materials, which can be used to fabricate highly efficient electrochemical systems, appears to be the fundamental requirement in fulfilling the energy needs of the society. Nanoscaling of electrodes for batteries has yielded great benefits in terms of the delivered capacity and rate capability. By reducing particle size to nano, the improved cathode/anode structure and the reduced Li+ (or Na+) diffusion path lengths can facilitate fast Li+ (or Na+) insertion/extraction reactions. Nanostrutured electrodes can also provide larger area to host cations as well as the spaces to accommodate expansion during cation hosting. Nevertheless, low volumetric efficiency and accelerated undesirable surface reactions also need to be considered when working with nanomaterials.

In the case of supercapacitors, most of the research efforts in the field of materials are directed toward the energy density improvement, and in order to get to this goal nanostructuring is of paramount importance. Capacitance is proportional to the number of active sites, and thus, high specific surface area (SSA) nanoporous materials are required as electrode materials. In this scenario, graphene and graphene-like carbons have become recently popular, however, activated carbons (ACs) still remain the materials of choice for commercial supercapacitor devices for cost reasons. In fact, the highly unfavourable mass production of nanomaterials is in general a major drawback for their industrialization both in supercapacitor and in battery fields.

In this talk we will present different nanomaterials as electrodes in Li and Na-ion batteries together with those for supercapacitors. The effect of these nanomaterials on the electrochemistry properties will be also discussed.

Nanotechnology and the Patent System

Luis Sanz Tejedor

Spanish Patent and Trademark Office (Ministerio de Energía, Turismo y Agenda Digital)
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The associated research and patent applications on Nanotechnology are very broad and include fields of science as diverse as medicine, organic chemistry, food science, materials science, physics, microfabrication, etc. The knowledge based economy has in IPR's a cornerstone on the strategy that companies follow to materialize knowledge and to appropriate the invention and its rents so it is crucial to establish a strategy to protect intangible assets, either by secrecy or by IPR's and in this case to keep in mind the specific ins and outs of the business the Patent system to obtains fruitful returns.

Patent legal systems are ready to face science and technology challenges. Spanish law has been recently adapted to these challenge.

IPR related indicators are also very useful when documenting trends and significance of innovation.

References

Figures

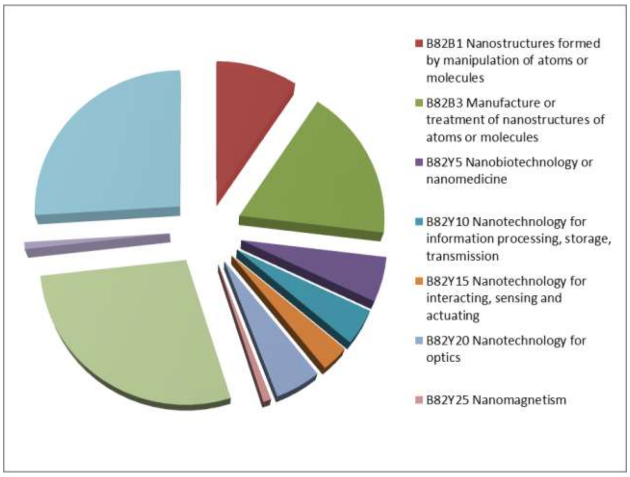

Figure 1: Publication of Nanotechnology patent documents worldwide in last 10 years


BOE BOLETÍN OFICIAL DEL ESTADO

I. DISPOSICIONES GENERALES

JEFATURA DEL ESTADO

Figure 2: New Spanish Patent Act from April, 1st 2017.

STC for Integrated Quantum Materials*
Quantum Information Science & Technology

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Abstract

The Vision of our Center is to create quantum sensors, quantum communication and quantum computers [1]. We bring together researchers at Harvard, Howard University and MIT, with public outreach through the Museum of Science, Boston. The Research Areas are: (1) Novel van der Waals Heterostructures, led by Philip Kim, (2) Discovery of New Topological Crystals, led by Joseph Checkelsky, (3) Topologically Protected Qubits, led by Amir Yacoby and Pablo Jarillo-Herrero, and (4) Quantum Networks with Engineered Solid-State Quantum Emitters, led by Marko Loncar. Active collaborations between research groups at different institutions promote multidisciplinary research. College Network schools - Bunker Hill and Prince George's Community Colleges, Mt Holyoke and Welllesley Women's Colleges, and Gaulladet University for the deaf and hard of hearing - encourage undergraduates to pursue careers in science and technology.

*Supported by NSF grant DMR-1231319.

References

[1] Center website: CIQM.harvard.edu

Figure 1: Science & Technology Center for Integrated Quantum Materials logo, showing a laser beam striking a nitrogen vacancy (NV) center in a diamond nanopillar, passing through a 2D material stack and a lens to illuminate electron spin and orbital motion (David Macaulay).

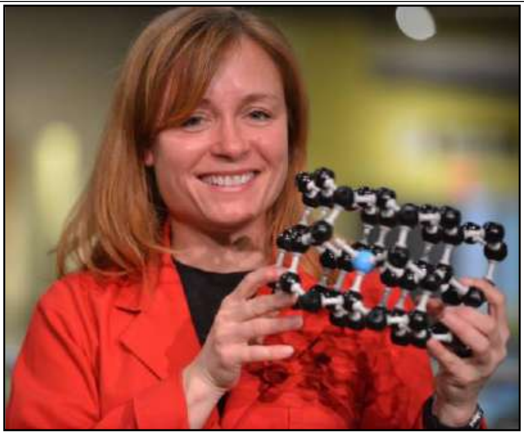

Figure 2: Museum of Science team member Karine Thate in a stage presentation on the Quantum Revolution in diamond created by nitrogen vacancy (NV) center qubits. Museum stage presentations reached over 11,000 children and adults.

NANOSPAIN2018 – ORALS

Spectrum of applications of world's highest resolution micro 3D printer: from research to industry

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Abstract:

The achievements of the two-photon polymeri-zation based world's highest resolution micro 3D printer "Photonic Professional GT" will be presented. The device offers a defined control on the feature sizes and resolutions ranging from nanometer to micrometer scale and acces-sible print area of ~ cm². This versatility has opened new frontiers in the field of photonics, optics, plasmonics, microfluidics, life sciences, bio-medical, microrobotics and many others. All this is made possible by the advancements in the software and hardware design of the printer as well as high level of materials research that enables the realization of ideas only with few mouse clicks.

The talk will focus on customer's applications in various fields. Prominent examples include photonic particle-accelerator [1], plasmonic color display [2], plasmonic nanoantenna [3], microoptics/micro-lenses, metamaterial absorbers [4], photonic wire bonding [5] etc.

All these excellent achievements were possible only because of a precise control on the geometry and surface of the printed objects at sub-micron level. The decade of trusted use of this technology has found its way to several industrial applications as well. This presentation will therefore, cover the latest advances utilizing this art of 3D microprinting that has made small things matter across the globe.

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[3] DOI: 10.1021/acsphotonics.5b00141
[4] DOI: 10.1002/adma.201300223
[5] DOI: 10.1109/JLT.2014.2373051

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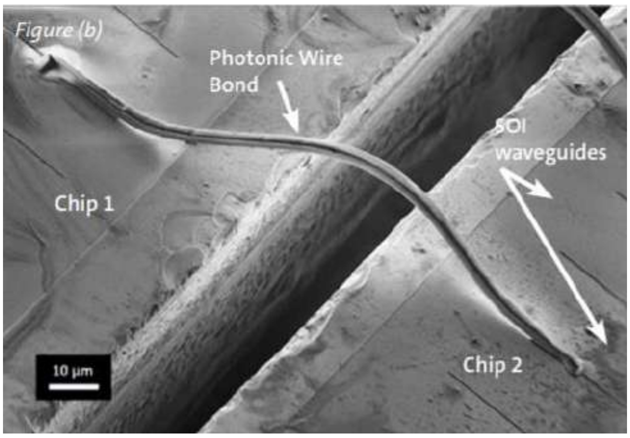

Figure 1: Photonic wire bonding: a novel concept for chip-scale interconnects. [5]

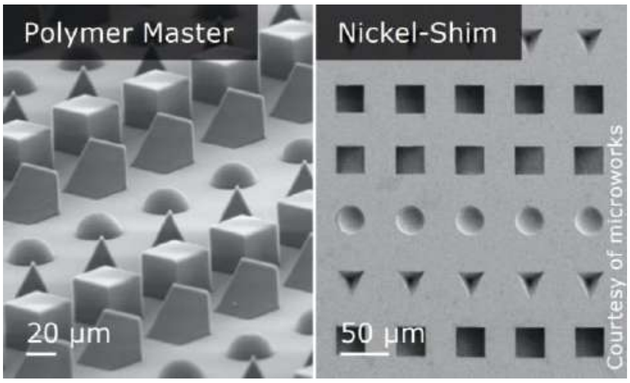

Figure 2: Example of mass replication via Ni-shim

Figure 3: Plasmonic color display [2]

PATENTING NANOTECHNOLOGY

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Patenting represents a pivotal step in the consolidation and future incentivisation of nanotechnology and nanoscience. Accordingly, the number of patent applications in these fields has increased exponentially over the last couple of decades – at the European Patent Office, the number of applications has quadrupled in this period.[1,2] The talk will focus on the basics and particulars of the patenting process as applied to nanotechnological and nanoscientific inventions and will provide guidance for inventors and companies on how to achieve proper patent protection for their developments.

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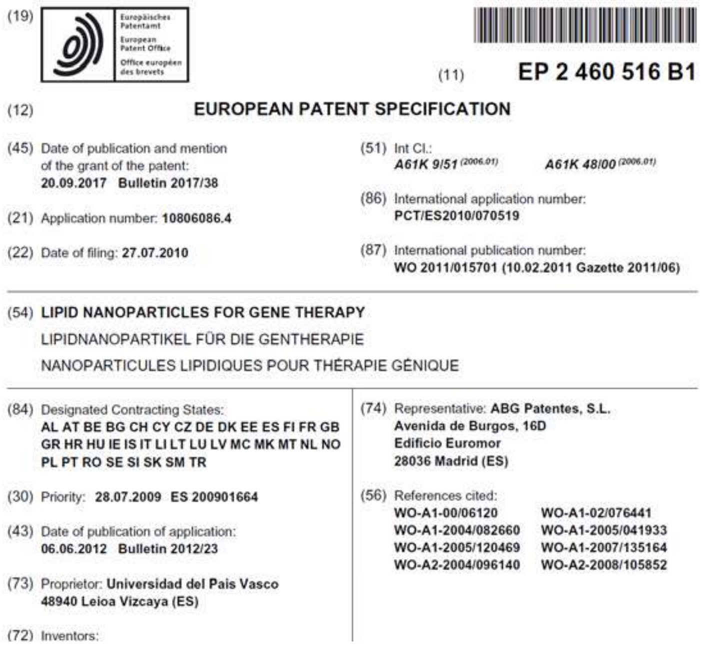
Figures



(19) Europäisches Patentamt / European Patent Office / Office européen des brevets

(11) **EP 2 460 516 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

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(22) Date of filing: **27.07.2010**

(51) Int Cl.: ***A61K 9/51*** (2006.01) ***A61K 48/00*** (2006.01)

(86) International application number: **PCT/ES2010/070519**

(87) International publication number: **WO 2011/015701 (10.02.2011 Gazette 2011/06)**

(54) **LIPID NANOPARTICLES FOR GENE THERAPY**
LIPIDNANOPARTIKEL FÜR DIE GENTHERAPIE
NANOPARTICULES LIPIDIQUES POUR THÉRAPIE GÉNIQUE

(84) Designated Contracting States: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR**

(30) Priority: **28.07.2009 ES 200901664**

(43) Date of publication of application: **06.06.2012 Bulletin 2012/23**

(73) Proprietor: **Universidad del Pais Vasco 48940 Leioa Vizcaya (ES)**

(72) Inventors:

(74) Representative: **ABG Patentes, S.L. Avenida de Burgos, 16D Edificio Euromor 28036 Madrid (ES)**

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Figure 1: European Patent for nanoscientific invention.

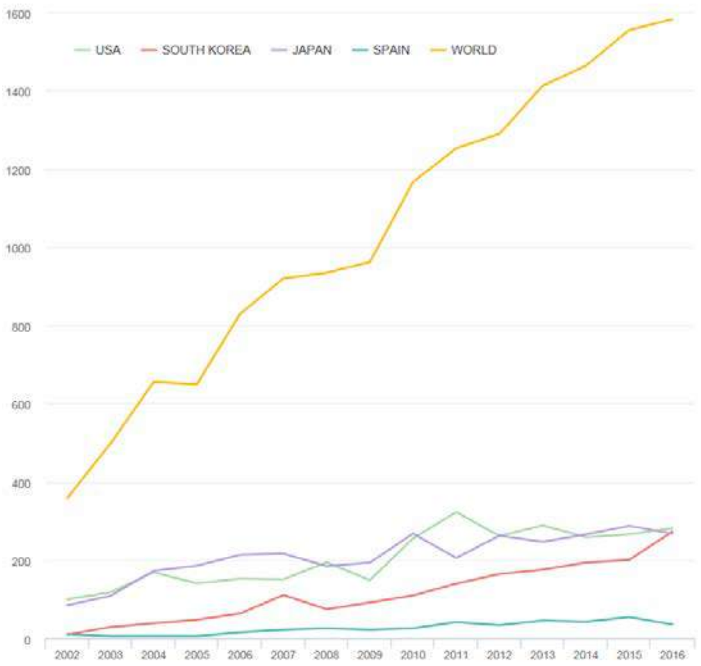

Figure 2: Nanotechnology European patent applications published from 2002 to 2016.[2]

Electrospun Nanofibers Containing Antimicrobial Peptides for Bio-film Prevention

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Abstract

Biomaterial-associated infections remain a serious concern in modern healthcare. The development of materials that can resist or prevent bacterial attachment constitutes a promising approach to dealing with this issue [1]. Promising solutions include electrospun fibres based on environmentally friendly polymers such as poly(acrylic acid) (PAA) and polyvinyl alcohol (PVA), which offer the advantage of their high surface area, chemical tenability and biocompatibility [2]. Antimicrobial peptides (AMPs) have been the focus of great interest in recent years owing to a low propensity for bacterial resistance, broad-spectrum activity, high efficacy at very low concentrations, target specificity, and synergistic action with classical antibiotics [1].

In this study, three potent AMPs (nisin, e-poly-lysine and lysozyme) were incorporated into PAA/PVA electrospun fibers via self-assembly for bio-film prevention. For this end, different immobilization conditions were employed. The specimen formulations were tested for: (i)surface characterization, by SEM, ATR-IR, nitrogen content, ζ-potential and fluorescamine assay; (ii)antibacterial activity with *Staphylococcus aureus* during two weeks, by agar diffusion and liquid incubation measurements of bacterial outgrowth; (iii)anti-biofilm activity by live/dead staining and SEM observation; (iv)mode of action by live/dead staining and (v)AMPs release profile by HPLC.

The amount of AMPs incorporated per unit mass of fibers was considerably larger when using ph7 conditions insteag of ph10 conditions and a higher degree of peptides loading was observed for lysozyme. The antimicrobial activity increased with AMPs content and time exposure, but the effect was much more apparent for lysozyme than for nisin and ε-poly-lysine. *S. aureus* decrease in CFU amounted to < 90% in liquid culture and over 99% for bacteria adhered to membrane surface. Figure 1 shows neat PAA/PVA meshes colonized by *S. aureus* (left) in contrast to PAA/PVA-Lysozyme meshes, which are essentially free of bacteria.
Based on the results of this study, PAA/PVA-Lysozyme immobilized nanofibers hold great promise for their use as alternatives to conventional wound dressing materials.

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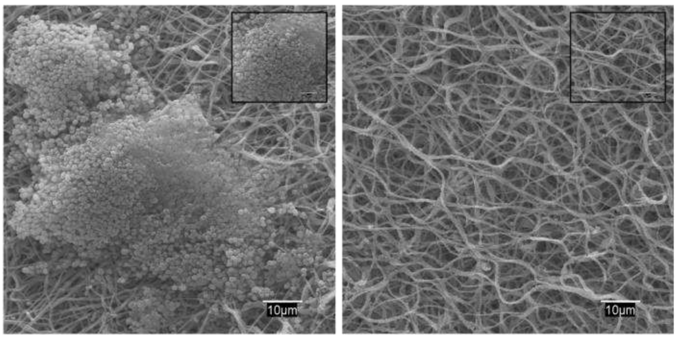

Figure 1: SEM micrographs of neat (left) and modified PAA.PVA (right) membranes in contact (14d) with cultures of *S.aureus*.

Optical spectroscopy signatures of single walled carbon nanotubes dispersed in degassed water without additives

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We study the intrinsic optical spectroscopy (UV-vis-NIR absorption, Raman and photoluminescence) signatures of single wall carbon nanotubes (SWNT) dispersed in degassed water without additives, so called ''eau de nanotubes'' (EdN). They are found to be very close to those of SWNT dispersed in aqueous suspensions stabilized with surfactants. Absorption peaks appear to be even slightly better resolved for EdN, suggesting sharper excitonic resonances, which is also supported by the Raman data. On the other hand, the photoluminescence signal is significantly weaker. These signatures suggest that SWNT are dispersed as individuals in degassed water, in a similar way single layer graphene was recently shown to be readily dispersable in degassed water [1-3].

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Layertronics – the layer localization control of topological states in bilayer graphene with a gate voltage

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L. Chico [5]
A. Ayuela[2]

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Experiments in gated bilayer graphene with stacking domain walls show a couple of topological gapless states protected by no-valley mixing. We investigate these states under gate voltages [1,2]. We find that the layer localization of the two states switches non-trivially between layers depending on the applied gate voltage magnitude. The control of the carriers localization in distinct layers along domain walls opens the possibility for the design of layertronic devices, which could be exploited in addition to other degrees of freedom, like valley, spin and charge, in graphene-based electronics. The localization analysis is performed using atomistic models, which allow us to elucidate the origin of topological gapless states, i.e., to indicate the bands of single-layer graphene they arise from. Based on this analysis we provide a model Hamiltonian with analytical solutions, which explains the layer localization as a function of the ratio between the applied potential and interlayer hopping.

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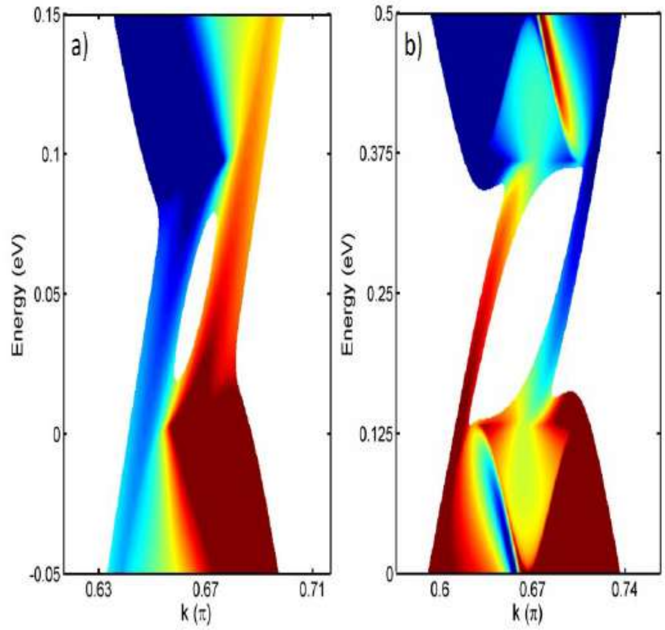

Figure 1: Topological gapless modes of bilayer graphene with stacking domain wall for two values of the gate voltage, V=0.1 eV (a) and V=0.5 eV (b). Color reflects the localization in top (blue) or bottom (red) layer.

Toxicological profile assessment of ENMS for polymer industry in the context of NanoDesk SUDOE project

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New developments have arisen based on the use of the nanotechnology, which brings innovative opportunities to the plastic industry, enabling the development of materials with new functional properties.[1, 2]
The incorporation of nanofillers opens an opportunity for developing innovative and high performance of polymer based materials (volume and surface properties; dimensional and chemical stability; photocatalytic, optical, electrical and thermal properties, among others). However, nanoparticles (NPs) can be dangerous due to its own toxicity, or because of the toxicity derived from the molecules that functionalize it. Therefore, it is necessary to ensure that the ENMs use does not pose risks to health or the environment.[3]
In this context, the main objective of the NanoDesk project is to promote nanotechnology as key enabling technology to develop novel added value plastic materials based on the use of engineered nanomaterials (ENMs). The project addresses current barriers limiting the use of ENMs by the development of tools to support decision making, including applications to identify proper nanofillers for targeted applications, advanced browsers to improve the access to information on applications and safety issues, on line tools to characterize the toxicological profile and exposure potential to relevant nanomaterials, as well a complete observatory on the safety and applications of nanostructured polymers.
We define the toxicological profile of the selected ENMs (metal nanoparticles and metal oxides, carbon based materials, nanoclays). To assess ecotoxicological impact, we performed acute toxicity assays with *Daphnia magna*, using immobilization (EC_{50}) as toxicological endpoint. For the toxicity assessment, we performed MTT Proliferation Assay to study ENMs cytotoxicity (cellular damage), and the Comet Assay in the case of genotoxicity (DNA damage). In both procedures, two types of cell lines were used: the adenocarcinomic human alveolar basal epithelial cells A549; and the spontaneously immortalized aneuploid human keratinocyte cell line HaCaT.

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Figures

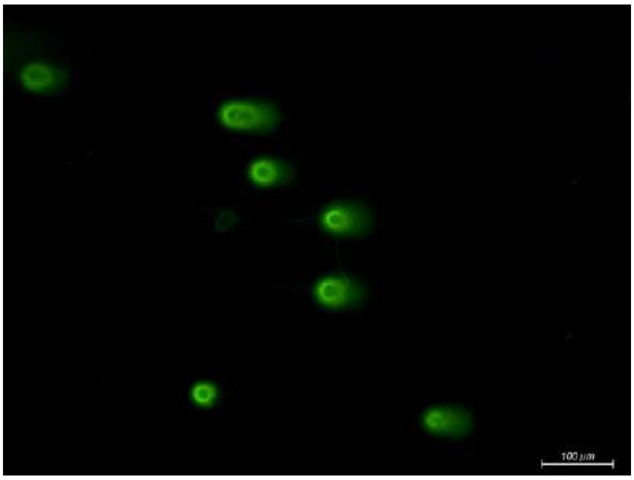

Figure 1: Fluorescence Microscopy (LAS CORE™, LEICA Microsistems) image example: TiO^2 studied nanoparticle by Comet Assay. Long comet tails extending toward the anode were observed as an indicator of DNA damage.

New approaches towards surface-supported two-dimensional covalent organic frameworks.

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Dynamic covalent chemistry (DCC) has a central role in organic synthesis due to its ability to form products which are otherwise not easily accessible through classic synthetic routes. DCC is a versatile approach that allows harvesting one desired product out of a combinatorial library through selection of well-defined and controlled equilibrium conditions. **Dynamic polymers** have the ability to break and reform their linkages and thus, to adapt their structures and constitutions by reorganization of their building blocks under thermodynamic conditions.[1] As a consequence, they have opened the possibility to design responsive materials by combining DCC and polymer science. The formation of imine bonds and the condensation of boronic acids are simple yet efficient DCC reactions, which are extensively used in the synthesis of **two-dimensional covalent organic frameworks (2D-COFs)**, an appealing new family of materials marked by crystalline extended organic architectures in which the building blocks are linked together by strong covalent bonds. Under optimal conditions, these reactions yield at the interface between a liquid and a solid substrate and under ambient conditions extended porous networks that compete with supramolecular systems, both in terms of domain size and structural quality.[2] By associating molecules of appropriate structure and functionality in a covalent manner, robust sheets of material with a well-defined composition and porosity are created.

In this work, atomically-flat conductive substrates, such as highly oriented pyrolytic graphite (HOPG), serve as support for the adsorption and self-assembly of the molecules, as well as prevent the stacking of the layers; and scanning probe microscopies (SPM), such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), are used to visualize the adsorbates. It will be shown how this methodology allows for a close monitoring of the *in situ* reaction with (sub)molecular resolution, which in turn grants precise control over the synthetic process. It will be exemplified how SPM techniques are a great asset to the design and investigation of 2D materials.[3]

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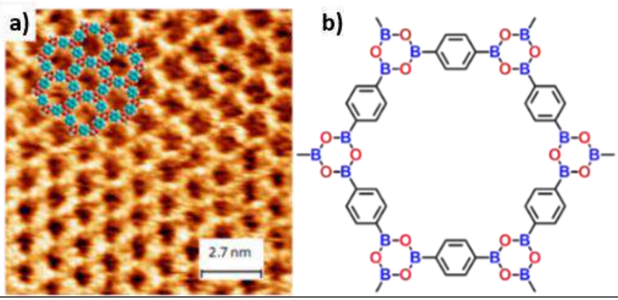

(a) STM image of a 2D-COF on graphite synthesized from 1,4-phenyldiboronic acid with superimposed molecular model; and (b) chemical structure of the cyclic unit.

Mastering Contrast Agents in a Single Structure for T_1-T_2 Dual Magnetic Resonance Imaging

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Introduction. Signal Intensity (SI) in Magnetic resonance imaging (MRI) depends on longitudinal (T_1) and transversal (T_2) relaxivity times.[1] Unfortunately, the intrinsic contrast changes associated to a pathologic condition are often too limited for accurate diagnosis. Here, MRI contrast agents (CA) improve image resolution based on their selective accumulation in the Region Of Interest.[2] These CAs are classified as positive (T_1-weighted) or negative (T_2-weighted) image contrast promoters. The acquisition of MRI weighted in T_1 and T_2 could improve the safety of diagnosis.[3] In this context, it has been reported that Prussian Blue (PB) derivatives with general molecular formula $K_xGd_{1-x}(H_2O)_n[Fe(CN)_6]$ and nanosized crystallites present high performance as dual T_1-T_2 CAs.[4] Unfortunately, their clinical use is precluded by the partial solubility in physiological medium. In this work, to protect $Gd(H_2O)_4[Fe(CN)_6]$ nanoparticles we have coated them with a thin amorphous silica shell by polymerizing the silicate at neutral pH, obtaining an stable CA for *in vivo* MRI.

Results and Discussion. The combination of Gd and Fe magnetic centers closely packed at the same crystalline structure leads to a magnetic synergistic effect, which results in an outstanding improvement of longitudinal relaxivity with regards to soluble Gd^{3+} chelates, whilst keeping the high transversal relaxivity inherent to iron oxide nanoparticles. This CA improves positive and negative contrast in T_1- and T_2-weighted MR images, both in *in vitro* and *in vivo* systems. Furthermore, this novel hybrid presents a high biosafety profile and has strong ability to incorporate organic molecules on surface, displaying great potential for further clinical application.

Conclusion. With regards other proposed T_1-T_2 dual mode CAs, these nanoparticles present very homogeneous composition and constant Gd:Fe atomic ratio, providing reproducible quality in MRI signal.

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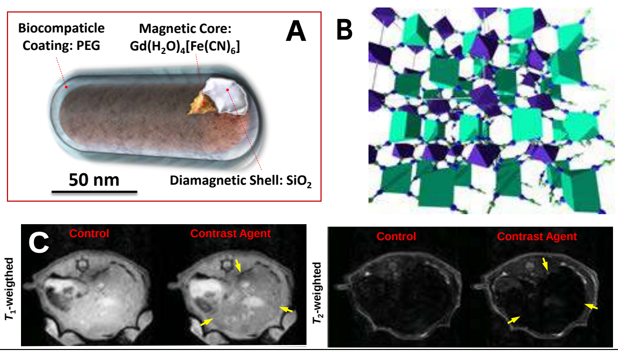

Figure 1: (A) Artistic representation of Gd-PB nanoparticle protected with a silica shell. (B) Network topology of $Gd(H_2O)_4[Fe(CN)_6]$. (C) *In vivo* coronal T_1- and T_2-weighted images acquired from a male Sprague-Dawley rat at 7 T magnetic field.

Exploring the potential of graphene nanomaterials as carriers for oil compounds: an *in vitro* toxicity approach

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Complex mixtures of pollutants are usually found in the aquatic environment. Polycyclic aromatic hydrocarbons (PAHs) are prioritary pollutants and main constituents of the water accommodated fraction (WAF) of oil. Graphene nanoplatelets can adsorb organic compounds thus being potentially useful in oil spill remediation. However, they could also act as vehicles of organic contaminants to aquatic organisms (the so-called "Trojan horse" effect) (1, 2). This study aimed to evaluate the potential "Trojan horse" effect of graphene nanoplatelets (graphene oxide (GO), GO-polyvinylpyrrolidone (GO-PVP) and reduced GO-PVP (rGO-PVP)) with adsorbed oil compounds from naphthenic North Sea crude oil WAF (3) using *in vitro* toxicity assays in hemocytes of marine mussels (4). Two approaches were tested to obtain graphene nanoplatelets with adsorbed oil compounds: filtration and centrifugation. Hemocytes were exposed to a wide range of concentrations of GO, GO-PVP and rGO-PVP with and without adsorbed oil compounds and to a series of WAF dilutions. After 24 h exposure, cell viability (MTT assay) and ROS production were assessed (4). Centrifugation (270*g* for 30 min) successfully separated WAF solution from graphene nanoplatelets with adsorbed oil compounds. This procedure was thus used for *in vitro* toxicity testing. Exposure to WAF decreased cell viability and increased ROS production in hemocytes starting at 25% WAF. In line with previous studies (4), GO, GO-PVP and rGO-PVP nanoplatelets were moderately toxic to mussel hemocytes and produced a significant increase in ROS production. In exposures to graphene with adsorbed oil compounds, hemocytes viability decreased at similar concentrations as in exposures to nanoplatelets alone. However, ROS production increased in hemocytes exposed to lower concentrations of graphene with adsorbed oil compounds (10 mg/L) compared to nanoplatelets alone (25 mg/L), indicating that adsorbed oil compounds increase nanoplatelets toxicity. In conclusion, a protocol to obtain graphene nanoplatelets with adsorbed oil compounds was established. Nanoplatelets with and without adsorbed oil compounds showed similar cytotoxicity to hemocytes but the ones with adsorbed oil compounds increased ROS production earlier, indicating that graphene nanoplatelets may act as "Trojan horse" carriers of oil compounds. This work was funded by the EU H2020 GRACE project (grant 679266), Spanish MINECO (project NACE, CTM2016-81130-R), Basque Government (consolidated research group IT810-13) and University of the Basque Country (UFI 11/37).

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In situ detection of the protein corona in complex environments

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Colloidal nanoparticles (NPs) may undergo drastic changes *in vivo* by the formation of a protein corona [1]. The dynamic development of protein corona formation has been studied extensively by mass spectroscopy or other techniques. Such measurements have been performed in relevant solutions such as blood4, which, however, requires extraction of the NPs and removal of unbound excess proteins, leading to a loss of the equilibrium properties. Alternatively, protein corona formation can be observed based on measuring the associated increase in the NPs' hydrodynamic radius and reduction in diffusion coefficient. In case only protein–NP complexes, but no free proteins, are subject to diffusion coefficient measurements, protein corona formation can be quantified *in situ*, without removal of excess proteins. Several optical methods, such as fluorescence correlation spectroscopy (FCS) or depolarized dynamic light scattering (DDLS), have been established for *in situ* quantification based on diffusion coefficient measurements. However, in complex media such as blood or even tissue, optical detection suffers from light scattering. Unfortunately, the *in vivo* corona cannot be completely emulated by the corona formed in blood. Thus, *in situ* detection in complex media, *i.e.*, ultimately *in vivo*, is required. In this work, we present a non-optical methodology for determining protein corona formation in complex media. NPs are labeled with ^{19}F and their diffusion coefficient is measured using ^{19}F diffusion nuclear magnetic resonance (NMR) spectroscopy, recording a diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY) experiment [2]. Herein we propose the use of ^{19}F diffusion NMR to observe changes in hydrodynamic radius of NPs upon adsorption of proteins in solution and also in complex media such as blood. For this purpose, three types of Au NPs labeled with fluorinated polyethylene glycol (PEG) ligands were synthesized. Two of them contained additional PEG chains bearing either $-CO_2H$ or $-NH_2$ head groups and the third type was further coated with poly(isobutylene–alt-maleic anhydride) (PMA), which in water also presents $-CO_2H$ groups at its surface. The diffusion of these nanoparticles was studied in the presence of several proteins, blood, plasma and cells.

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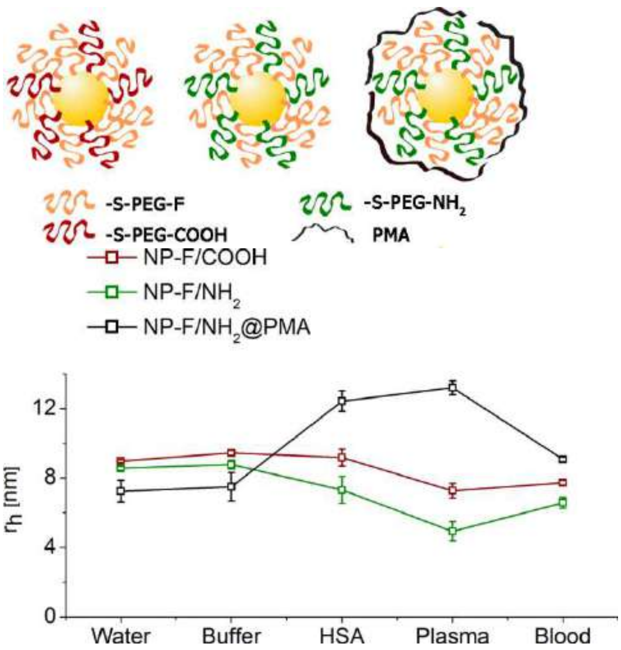

Figure 1: Illustration of the ^{19}F-labeled NPs and size measurements in different media.

SWIR luminescence nanothermometry for biomedical applications

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High resolution thermal sensing and bioimaging at the cellular level and in animal models (*in vivo* applications) is interesting for both early diagnosis and controlled treatment via photothermal conversion of several diseases, including cancer. Despite excellent *in vitro* results have been obtained with visible emitting luminescent nanothermometers [1], their application for *in vivo* studies is very limited due to the reduced penetration depth of visible light in biological tissues. This can be overcome if materials with emission and absorption bands lying in the so-called biological windows (BWs) (650-1350 nm) [2] are used, where tissue scattering and absorption are minimized. However, still the quest for a material that maximizes the luminescence quantum efficiency in this region, allowing for high penetration depths in the body is a matter of special interest. Despite all this work, the number of studies exploring the possibilities of longer emission wavelengths in luminescence thermometry are scarce. This includes those lying in the so called short-wavelength infrared (SWIR) that extends from 1.35 to 2.3 µm. SWIR light transmits more effectively (up to three times) through specific biological tissues (oxygenated blood and melanin-containing tumours), achieving higher penetration depths due to the reduced tissue absorbance and scattering in this region [3]. Here, we analyse the possibilities for temperature sensing purposes and the development of primary thermometers with the emissions in the SWIR region generated by Er^{3+}, Tm^{3+} and Ho^{3+} ions in different host matrices, including fluorides ($NaYF_4$), oxyfluorides (NaY_2F_5O), simple oxides (Lu_2O_3) and complex oxides ($KLu(WO_4)_2$). The thermometric responses of these particles are compared with those shown by other Ln^{3+}-doped nanoparticles operating in the visible, and in the BWs, and demonstrated the potentiality of SWIR emitting nanoparticles for temperature measurements in biological tissues by using chicken breast meat. The results indicate that SWIR emitting nanoparticles are good candidates for luminescent nanothermometry in biomedical applications.

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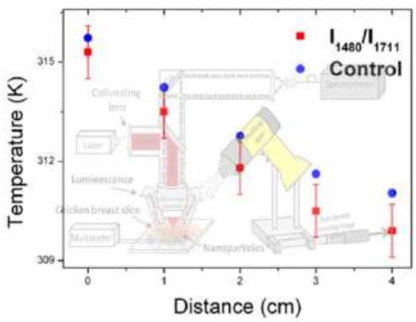

Figure 1: Scheme of the setup used in the temperature sensing experiments and results obtained with luminescent nanoparticles and thermocouple (control).

Passion fruit-like nano-architectures: enabling the clinical translation of metal nanomaterials

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Abstract

Noble metal nanoparticles (NPs) hold the promise to shift the current medical paradigms for the detection and therapy of neoplasms due to their intriguing physiochemical properties. Nonetheless, no noble metal NPs for cancer theranostics are currently available in the market. Clinical translation is mainly hampered by the issue of metal persistence in organism after the designed action, which increases the likelihood of toxicity and the interference with common medical diagnoses. Size reduction of NPs to ultrasmall regime (1-6 nm) promotes excretion by the renal pathway, yet most of their appealing properties are lost or severely altered.[1] We have proposed a smart approach to circumvent this issue by synthesizing biodegradable silica nano-architectures (NAs) of 100 nm containing 3 nm noble metal NPs embedded in a polymeric matrix: the passion fruit-like nano-architectures.[2,3] NAs mimic the optical behaviour of 30 nm NPs while affording biodegradation to kidney clearable building blocks in less than 48h. Their potential therapeutic and diagnostic applications have been demonstrated, respectively, *in vitro* towards pancreatic cancer cells, and *ex vivo* through combined US/photoacoustic imaging.[4,5] Furthermore, *in vivo* excretion assessment have been performed and the promising preliminary results will be discussed.

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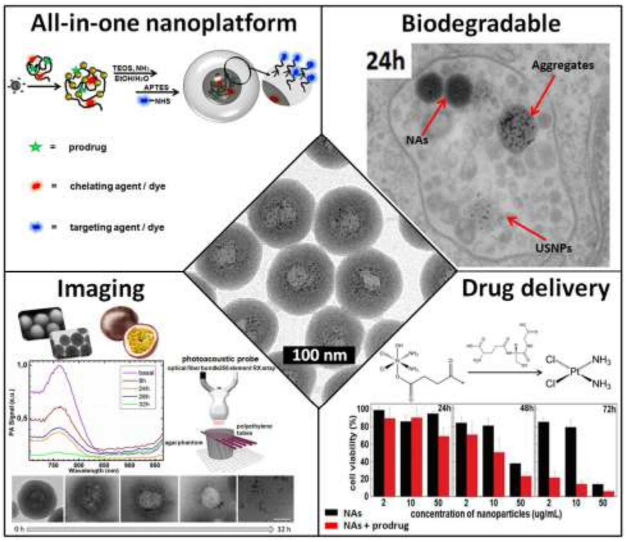

Figure 1: Typical TEM image of passion fruit like nano-architectures (NAs) (center) and their main features. Clockwise from top-left: scheme of the production for all-in-one nanoplatforms, biodegradation of NAs in cellular environment, PA imaging during degradation in phantoms, and in vitro drug delivery of endogenous GSH-triggered cisplatin prodrug.

Local Electronic Structure of a Single-Layer Porphyrin-Containing Covalent Organic Framework

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We have characterized the local electronic structure of a porphyrin-containing single-layer covalent organic framework (COF) exhibiting a square lattice. The COF monolayer was obtained by the deposition of 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMA) and 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAPP) onto a Au(111) surface in ultrahigh vacuum followed by annealing to facilitate Schiff-base condensations between monomers. Scanning tunneling spectroscopy (STS) experiments conducted on isolated TAPP precursor molecules and the covalently linked COF networks yield similar transport (HOMO–LUMO) gaps of 1.85 ± 0.05 eV and 1.98 ± 0.04 eV, respectively. The COF orbital energy alignment, however, undergoes a significant downward shift compared to isolated TAPP molecules due to the electron-withdrawing nature of the imine bond formed during COF synthesis. Direct imaging of the COF local density of states (LDOS) *via* d*I*/d*V* mapping reveals that the COF HOMO and LUMO states are localized mainly on the porphyrin cores and that the HOMO displays reduced symmetry. DFT calculations reproduce the imine-induced negative shift in orbital energies and reveal that the origin of the reduced COF wave function symmetry is a saddle-like structure adopted by the porphyrin macrocycle due to its interactions with the Au(111) substrate.

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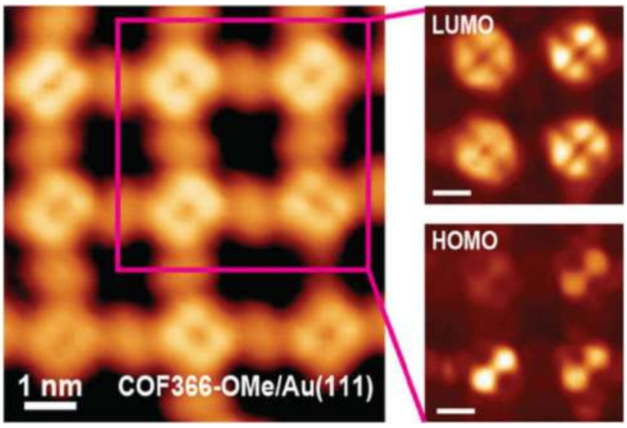

Figure 1: STM images of the single-layer covalent organic framework and the wavefunction distribution of the LUMO and HOMO states.

Redispersion and Self-Assembly of C_{60} Fullerene in Water and Toluene

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Abstract

This work aims at assessing the influence of two different solvents, bidistilled water and toluene, on dispersions of carbon-based engineered nanomaterials, fullerenes, and their self-assembly behavior. The obtained self-assembled carbon-based materials were characterized using UV–vis spectrophotometry and transmission electron microscopy techniques. The results obtained were unexpected when toluene was used for dispersing fullerene C_{60}, with the formation of two different types of self-assembled structures: fullerene C_{60} nanowhiskers (FNWs) and a type of quasispherical nanostructure. The FNWs ranged between 1 and 6 µm in length, whereas the quasispherical fullerene C_{60} nanoaggregates ranged between 10 and 50 nm in diameter [1]. Aggregates obtained in toluene showed a well-formed crystal structure. When using water, the obtained aggregates were amorphous and showed a no well-defined shape. Their sizes ranged between 20 and 40 nm for nanosized structures and between 0.4 and 4.8 µm for micron-sized self-aggregates. Previous work [2] underlined that C_{60} shows very low solubility in water, whereas the solubility of C_{60} in toluene is 2.8 mg/mL, which is an important factor to take into account in our experiments and in further studies [3].

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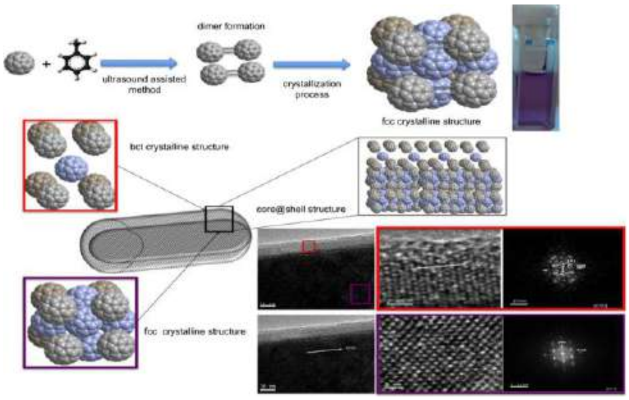

Figure 1: Graphical abstract: dimmer formation of FC_{60} redispersed in toluene, core-shell structure formation of FNWs, TEM, HRTEM images, growth indexes confirming fcc and bct crystalline structures.

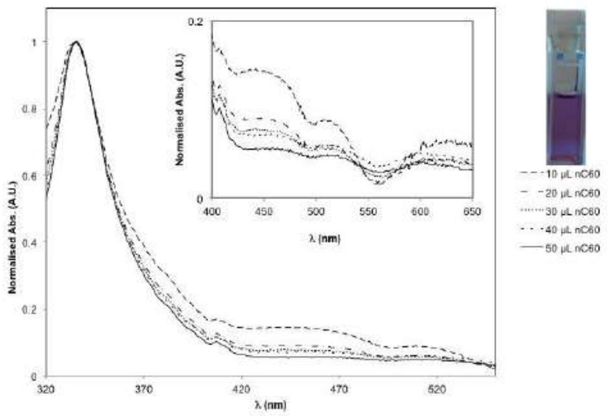

Figure 2: UV–vis normalized absorbance spectra of fullerene C_{60} in toluene at several concentrations. Inset: Enhanced image of the peak found at 407 nm. Naked-eye observation of C_{60} redispersed in toluene.

Reconfigurable Assemblies of Plasmonic Nanoparticles and Proteins for Biosensing

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Generating assemblies of gold nanoparticles with tailored localized surface plasmon resonance (LSPR) is a winning strategy for designing ultrasensitive biosensors [1] and photothermal nanomedicines [2]. If these assemblies changed their structure as a function of external stimuli, they could adapt their LSPR to variations in physicochemical cues. Such materials could be programmed to detect changes in their environment and emit signals and/or exert a therapeutic effect autonomously.

In this contribution I will show a new method for assembling gold nanoparticles with tailored near-infrared (NIR) LSPR that sense changes in chemical cues and reconfigure their structure accordingly [3]. It is based on adding biotin-binding proteins to a solution of citrate-capped nanoparticles under pH-controlled conditions. The assemblies show a chain-like morphology, which results in a new NIR LSPR that is intimately related to the number of nanoparticles within the assemblies (Figure1). Furthermore, the proteins in the assemblies retain their biotin-binding properties, which makes it easy to decorate the assemblies with biotinylated molecules such as enzymes. The assemblies reconfigure into smaller clusters when the pH of the solution or the concentration of thiolated molecules increases, and therefore they can be programmed to adapt their NIR absorption as a function of these parameters.

The LSPR of the assemblies is directly related to the concentration of proteins added to the nanoparticles. This observation has allowed us to design a new signal generation mechanism for biosensing based on changing the concentration of neutravidin, and therefore the LSPR of the assemblies, with an immunoassay that uses biotinylated antibodies as biorecognition elements. Instead of using bulky spectrophotometers or unreliable naked-eye visualization for detecting changes in the extinction spectrum of the nanoparticles we have designed a new type of paper transducer that enables detecting such changes with an augmented reality app [4]. With this approach, we have been able to detect the model analyte C-reactive protein with a lower limit of detection than a conventional, non-portable ELISA.

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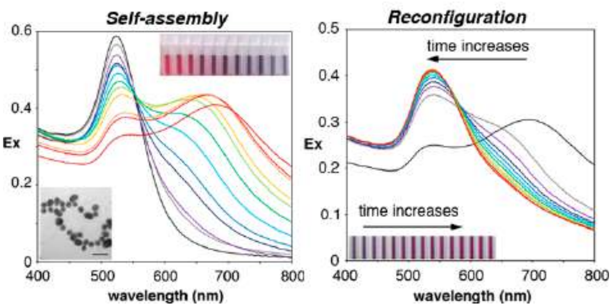

Figure 1: Figure 1: Assembly and reconfiguration of gold nanoparticles with chain-like morphologies. The key aspect to assemble the colloids is adding biotin-binding proteins at different concentrations. This can be used to generate plasmonic signals in biosensors using biotinylated antibodies as recognition elements.

“Smart multifunctional GLA-nanoformulation for treating Fabry disease”

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Abstract (Century Gothic 11)

Lysosomal storage disorders (LSD) diseases are a group of rare diseases that currently lack a definitive cure. LSD incidence is about 1:5,000 - 1:10,000, representing a serious global health problem. One relevant LSD is the Fabry disease (FD), in which the deficiency in α-Galactosidase A (GLA) enzyme activity results in the cellular accumulation of neutral glycosphingolipids, leading to widespread vasculopathy with particular detriment of the kidneys, heart and nervous system. The current treatment for FD is the Enzyme Replacement Therapy (ERT), in which free GLA recombinant protein is administered intravenously to patients. ERT exhibits several drawbacks mainly related to the instability, high immunogenicity and low efficacy of the exogenously administered GLA to cross biological barriers, such cell membranes and blood brain barrier (BBB). In this scenario, a correct nanoformulation of the GLA enzyme is foreseen as a critical step to improve the ERT.
Precisely, the aim of Smart-4-Fabry EU project (#720942) is to achieve excellent quality control over the assembly of the different molecular components of a new liposomal nanoformulation of GLA, nano-GLA, for the treatment of Fabry disease. Nanoformulated GLA has already shown to have better PK/PD profile than free GLA and higher efficacy in vivo [1]. Smart-4-Fabry project will advance nano-GLA from an experimental PoC (TRL3) to preclinical regulatory phase (TRL5-6). A one-step method based on the use of green CO_2, will be used for the manufacturing of this novel nanoformulation under GMPs [2]. The final GLA nanoformulation will have tailored transport of GLA through cell membranes and BBB

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Figures

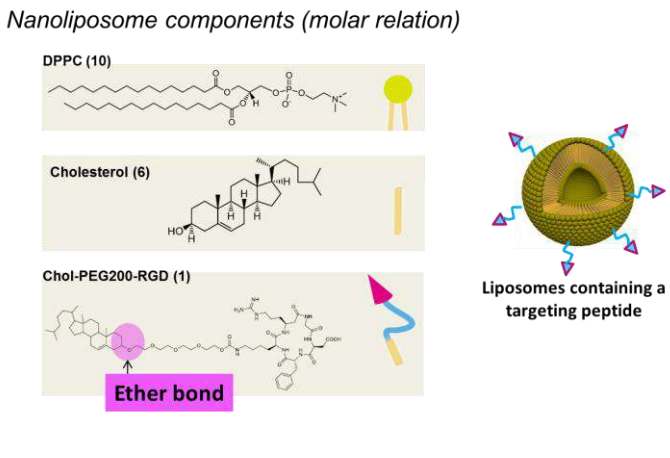

Figure 1: Modified (patent protected) lipids and lipsome strcuture

Anti-(bio) fouling Composite Membranes by Polyacrylic acid/Poly(vinyl alcohol) Layer

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Abstract

Development of the thin film and coating technologies (TFCT) made possible the technological revolution in ultrafiltration membranes and through it the revolution in water treatment sector in the end of the twentieth century [1]. Currently, TFCT along with nanotechnologies is the most promising for the development of almost all industries [2].
This work reports the use of a layer of polyacrylic acid-poly(vinyl alcohol) (PAA-PVA) electrospun fibers for the surface functionalization of a polysulfone (PSU) ultrafiltration membrane. The composite was stabilized by interfacial crosslinking after UV irradiation of the PSU support. The physicochemical properties of the resulting composites were determined by FTIR spectroscopy, water contact angle, surface zeta potential and pure water permeation measurements. The resistance to organic fouling was assessed using bovine serum albumin (BSA) and the antibacterial and antibiofilm performance of composite membranes was investigated using gram-negative *Escherichia coli* (*E.coli*) and gram-positive *Staphylococcus aureus (S.aureus)* strains. The bioassays were performed in static and cross-flow modes.
The results showed that PAA-PVA electrospun layers increased membrane hydrophilicity and enhanced water permeability. The resistance to organic fouling assessed using BSA showed that the presence of the electrospun layer increased the flux recovery ratio up to 80.2 % over the value of 29.4 % for PSU membranes. The antibacterial tests showed that PAA-PVA electrospun coating resulted in a considerable impairment for both bacteria, particularly for the gram-positive *S. aureus*, which was attributed to the chelating effect of PAA on the divalent cations stabilizing bacterial envelopes. The average reduction of colony forming bacteria for cells detached from the surface of composite membranes was about 1-log over their PSU counterparts. Composite membranes, benchmarked against the neat PSU membrane in 48h cross-flow experiments, showed good mechanical integrity and antimicrobial behavior under realistic conditions. Figure 1 shows neat PSU membranes colonized by *S.aureus* (left) in contrast to PAA/PVA-PSU membranes under cross-flow conditions.
This work demonstrates that top layer nanofiber composite membranes have the potential to be used as versatile materials to create ultrafiltration membranes with enhanced functionalities.

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Figures

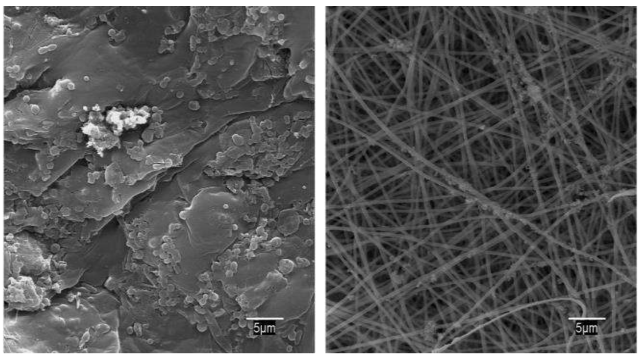

Figure 1: SEM micrographs of neat (left) and modified PSU (right) membranes under cross-flow conditions (48h).

Carbon Quantum Dots Fluorescent Labels Generated by Continuous Laser Fragmentation

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Carbon quantum dots (CQDs) are an outstanding material being used in applications such as bioimaging, cancer therapy or sensing [1]. To avoid cell damage for in vivo and in vitro imaging application, high purity samples are needed. Laser generation techniques ensure the high purity as no byproducts are needed in the process [2]. In this work it is proved the improvement in the generation efficiency of carbon quantum dots (CQDs) with a pulsed laser by applying for first time with this material a cost effective flow jet configuration in the generation process, Fig. 1. Compared to the most used laser technique, the proposed set up achieves an increase of 15 % in production. Besides, the generated CQDs exhibit an increment in quantum yield of an order of magnitude and its photoluminescence keeps constant for long periods of time even after cell internalization. Fast internalization of less than 10 min without any need of extra processing inside three different cancer and healthy epithelial cells (oral epithelial cells, A-549 lung cancer cells and HT-29 colon cancer cells) is proved, oral epithelial cells in Fig.2 as an example. This features make them an excellent fluorescent label that can be used in any in vitro or in vivo fluorescence imaging application.

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Figures

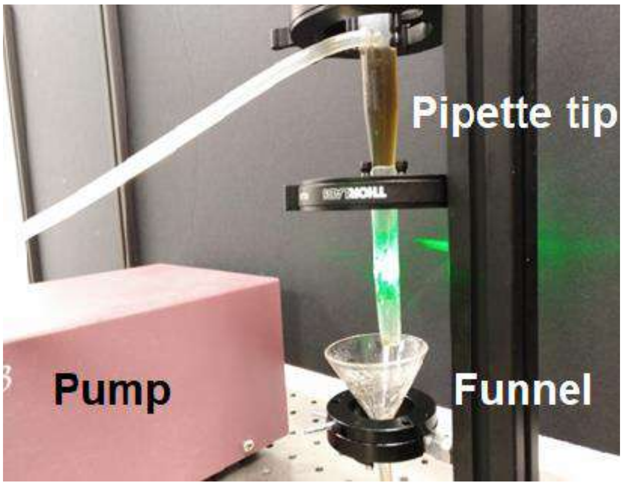

Figure 1: Flow jet experimental setup for continuous laser fragmentation of a carbon black microparticles suspension.

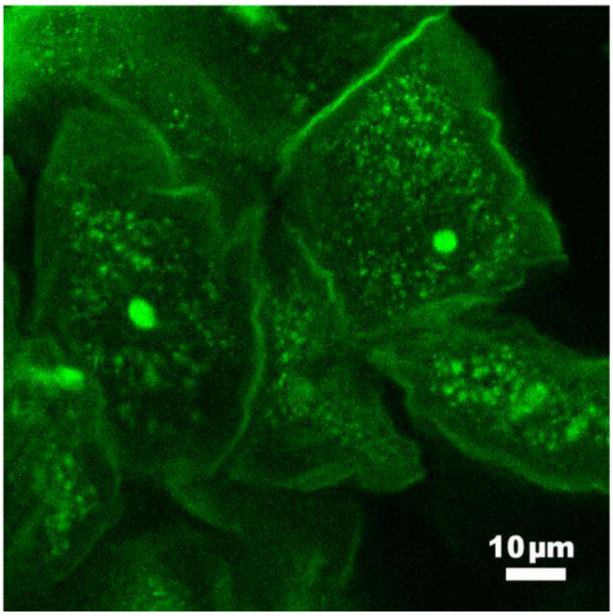

Figure 2: Example of fluorescence image of oral epithelial cells with complete internalization of the generated carbon quantum dots.

Nanosystems as biomimetic interfaces: a new strategy to predict drug candidate biophysical profile

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Abstract

Drug screening based in drug candidate profiling is now widely viewed as an important bottleneck in the drug development process. [1]
Considering that in physiological environment there will be reciprocal interactions between drugs and biological interfaces, such as cell membranes or plasma proteins, and from those interactions different pharmacokinetic profiles can be achieved [1, 2], nanotechnology could be a powerful tool to design new mimetic models. Biomimetic systems as nanoscale models provide useful tools to mimic different physiological environments that ally the measurement of fundamental biophysical properties to the ADMET profiling (absorption, distribution, excretion and toxicity at the membrane level) of newly synthesized drugs. [3] The application of different biophysical techniques (derivative spectroscopy; quenching of steady-state and time-resolved fluorescence; quenching of intrinsic fluorescence of human serum albumin; synchronous fluorescence; dynamic and electrophoretic light scattering; differential scanning calorimetry and small and wide angle x-ray diffraction) in a high-throughput screening approach allowed to predict that a newly synthesized drug MIT3 [4] has an ubiquitous location at the membrane level, presenting good membrane permeability properties and a good distribution in the therapeutic target. However, it presented bioaccumulation in non-therapeutic targets and under prolonged exposure conditions, the MIT3 may cause membrane toxicity as concluded by impairment of membrane biophysical properties. Thus, all this gathered information is intended to give drug discovery researchers some tools to support decisions related to modifications of the drug chemical structure to improve drugs' properties and thus increase the probability of success in the process of drug discovery.

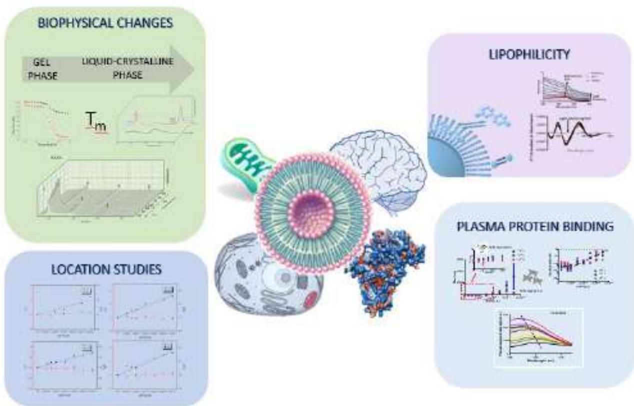

Figure 1: Representative summary image of the research developed

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NanoMONITOR- A new real-time monitoring system to support the risk assessment of ENMs under REACH

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The evaluation of the potential impact of ENMs in human health and the environment requires data on both effects and exposure.

In terms of exposure potential, the vast majority of studies are focused on workplace areas, where inhalation is the most common route of exposure. The skin has also been investigated, however, most studies have shown little to no transdermal ENMs absorption (Karjalainen et al, 2012).

In contrast to occupational exposure, current studies focused on the environmental release of ENMs and exposure to ENMs in areas other than industrial settings (e.g. urban areas) are scarce, which is mainly due to the lack of techniques to quantitatively monitor ENM emissions to and concentrations in urban areas and/or the environment, and hence, very little is known about the presence, type, composition and form of released ENMs.

To cope with this situation, the LIFE project NanoMONITOR (LIFE14 ENV/ES/000662) has developed an on-line information system consisting in two elements:

- A software application to support the acquisition, management and processing of data on the concentration of ENMs
- A new monitoring station prototype to support the outdoor and indoor monitoring of airborne ENMs.

Moreover, a new guidance on the sampling methods and analytical techniques for the measurement and monitoring of ENMs in the environment has been developed to support the selection of adequate sampling and monitoring procedures and techniques to characterize the concentration of ENMs in heterogeneous environments, including industrial settings, indoor and outdoor areas in urban locations and natural environments.

Up to 4 monitoring stations (figure 1) equipped with a measurement device optimized for continuous sampling of nanosized (1 to 100 nm in diameter) and ultra-fine airborne particles (10 to 300 nm in diameter) in indoor workplaces and outdoor environments have been developed, providing data on the number concentration (number / cm3), mass concentration (mg/cm3), lung deposited surface area (µm2/cm3), and average particle diameter (nm).

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Figures

Figure 1: NanoMONITOR Station

Figure 2: NanoMONITOR acquisition software

Low energy heating system based on Joule effect for electric vehicles

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Electric vehicles require specific thermal management solutions because their motors and batteries do not create heat in the same way as internal combustion engines. Up to 25% of the potential electric vehicle's range is reduced due to the use of current HVAC (heating, ventilation, and air conditioning) technologies. The main objective is the reduction of at least 50% of energy used for passenger comfort (<1,250 W) and at least 30% for component cooling in extreme conditions with reference to electric vehicles currently on the market.

Joule heating is the process by which the passage of an electric current through a conductor releases heat. The amount of heat release is proportional to the square of the current. Heating fabrics and panels are being develop aiming to achieve an efficient heating in the cabin. Heating is achieved with low energy consumptions. Latest results will be presented in the workshop.

Figures

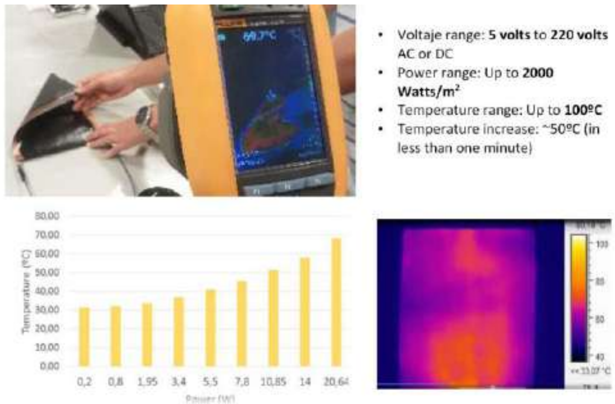

Figure 1: Figure 1: Jospel heating fabric and panels

The JOSPEL project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement nO 653851. The sole responsibility for the content of this presentation lies with the JOSPEL project and in no way reflects the views of the European Union.

Tunable performance of manganese oxide nanostructures as MRI contrast agents

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Magnetic resonance imaging (MRI) is a medical imaging technique perfectly suited for human healthcare applications. The lack of ionizing radiations, its high spatial/anatomical resolution and non-invasiveness make it an attractive tool for diagnostic purposes and to follow the progression of a disease/treatment.[1] To date the main limitation of MRI is its low sensitivity compared to radioactive-based and optical imaging modalities. To increase its sensitivity, contrast agents (CAs) are administered in about 50% of scans.[2] Clinically used CAs are based on a paramagnetic ion, Gd3+, that due to its toxicity has to be administered strongly chelated to limit its interference with biological proceses.[3] Other species are being studied as potential substitutes for Gd3+ chelates. MnO2 nanostructures present several advantages over traditional Gd chelates. First, Mn is less toxic than Gd. Also, MnO2 is not particularly active by MRI. This means that once administered it won´t produce significant changes in MR images. However, MnO2 is very sensitive to biologically relevant conditions. For example, under deregulated redox conditions, MnO2 will be easily reduced into Mn2+ which is highly paramagnetic and significantly enhances T1w MR signal.[4,5] This OFF-ON MR behavior can be exploited for diagnostic purposes. In this talk the synthesis and functional characterization of several MnxOy nanostructures will be discussed as well as their combination with reporter molecules for other imaging techniques as a step further towards multimodal and unequivocal imaging diagnosis.

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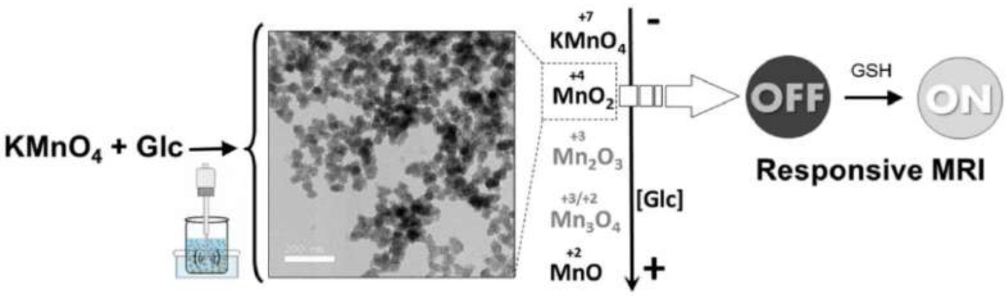

Figure 1: Schematic representation of the aim and results of this work.

CeO_2 nanoparticles as safe CT X-ray contrast imaging agents

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Use of X-ray computed tomography (CT) has increased dramatically over the last years in many countries owing to its availability, low cost and high resolution. An estimated 82 million scans were performed in the U.S. in 2016. However, a main concern about CT scans is the exposure to ionizing radiation. One study estimated that as many as 0.4% of current cancers in the U.S. are due to CTs performed in the past. Thus, an important issue is how to reduce the radiation dose during CT examinations without compromising the image quality. Contrast agents are regularly administered in order to improve image contrast. High Z-based nanoparticles have gained attention lately because they show notable advantages over commercial iodine-based compounds. For instance, they allow longer circulation times and deliver a large amount of heavy atoms[1]. In this work we present CeO_2 NPs as potential CT contrast agents. Cerium possesses high atomic number and electron density, it is biocompatible and CeO_2 NPs show antioxidant and anti-inflammatory properties, providing radioprotective capabilities [2]. In addition, given that the contrast enhancement depends both on the tube potential (kVp) and energy spectrum, Au-CeO_2 hybrides have also been prepared, increasing thus X-ray energy absorption range.

Firstly, it has been assessed the stability of the colloidal samples at the high concentrations required by the CT instruments (>100 mM), which are prone to aggregation and precipitation. In vitro CT results (Figure 1) indicate that, at equal molar concentrations, Ce-based NPs produce higher X-ray contrast than iodine. Additionally, we have observed that CeO_2 and Au-CeO_2 NPs act as a free-radical scavenger (Figure 2), reducing thus the radiation adverse effects of using metals in CT imaging [3].

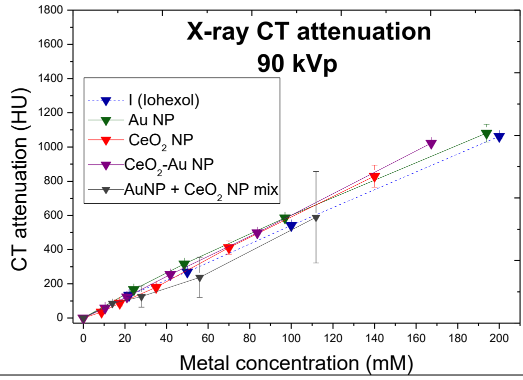

Figure 1: CT contrast (HU) as function of the metal concentration (mM).

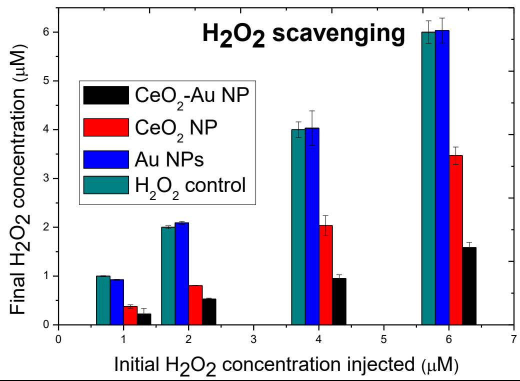

Figure 2: H_2O_2 scavenging tested with Amplex Red Assay

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Anisotropic Photo-Patterning of Fluorescent Nano-Fibers on Isotropic Surfaces: Control of Orientation, Position and Color

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The organization and patterning of optically active nanostructures on transparent surfaces is proposed using a photo-synthetic approach based on light-triggered self-assembly [1]. Using focused laser irradiation, we target to spatially and temporally control the self-assembly of a small molecule gelator (DDOA, 2,3-didecyloxyanthracene) into fluorescent nanofibers at the surface. The photocleavage of a soluble precursor can be triggered by visible light at 473 nm or two-photon excitation. A confocal microscope set-up is used for writing spatially defined nanostructures and image the photoactive patterns (Figure 1a). Patterning lines and rectangles occurs with a separate control of the nucleation and the growth by laser-scanning and successive wide-field illumination. The patterned nanofibers emit linearly polarized light. The technique provides also the unique possibility to pattern juxtaposed anisotropic micrometric patches of aligned nanofibers on an isotropic surface.
Furthermore, we propose FRET-assisted photo-patterning as a new strategy for a sub-micrometer scale color-tuning in self-assembled fluorescent nanoribbons formed by 2,3-dihexadecyloxy-9,10-diphenylanthracene [2]. The effective incorporation of guest-molecules that function as FRET-acceptors allows high energy transfer efficiencies, giving rise to a macroscopic modification of the emission color. Based on the same principle a simultaneous negative and positive laser-writing is feasible upon photo-oxidation of the acceptor molecules. This allows individual ribbons to be color-tuned locally at the microscopic level (Figure 1b).

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Figures

a) b)

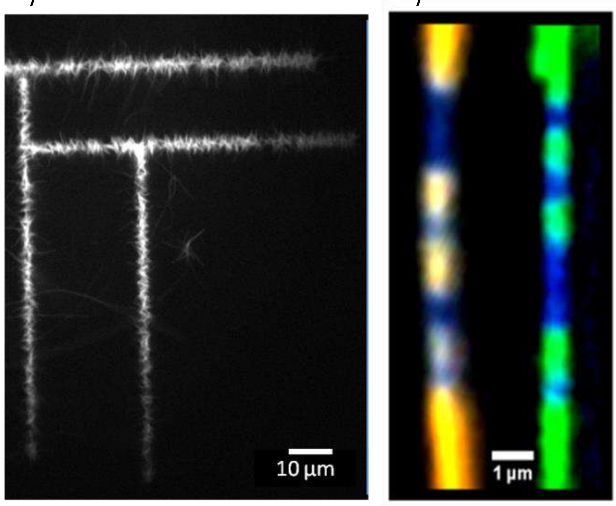

Figure 1: a) Lines of DDOA fibers obtained by repetitive line scans in xy and yx direction with a focused laser. Scale bar is 10 µm. b) Hyper-spectral maps of an orange and a green ribbon patterned in presence of ambient oxygen.

Funding: EC Marie Curie ITN project SMARTNET and Basque Government Postdoctoral Fellowship (L.G-R).

How Nature Indexing Helps You Find Nanotechnology Literatures and Data Efficiently

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Abstract

The exponential growth in nanotechnology has led to vast amounts of information and data being dispersed throughout various journals and patents making the acquisition of this information difficult. Furthermore, the lack of standardized nomenclature for nanomaterials is a huge challenge which makes seeking and transfer of scientific results a difficult task for researchers. There exists, however, a great demand for quick and curated information on nanomaterials, properties and applications. nano.nature.com known as Nano[1] was launched on 15 June 2016 as a non-journal type product under the Nature Research portfolio. It aims to provide highly indexed and structured information related to nanotechnology, including materials, properties, applications and preparation methods, derived from peer-reviewed journals at the article level and in manually curated nanomaterial summaries that compile data from multiple sources.

This talk will illustrate how Nano can aid nanotechnology research communities to obtain fast and precise insights into the wealth of nanotechnology based scholarly knowledge via use case scenarios and provide the latest developments.

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Figures

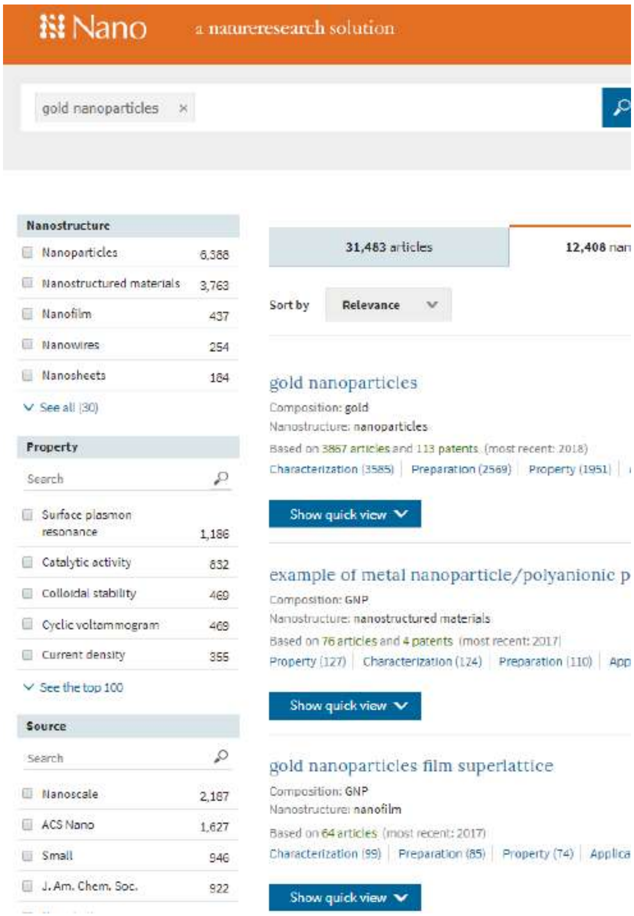

Figure 1: A preview of Nano searching for gold nanoparticle information.

Simultaneous advanced microscopies for cellular dynamics

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Abstract

Atomic Force Microscopy (AFM) has been combined with different fluorescence microscopy techniques [1]. However, the vast majority of the proposed set-ups does not enable simultaneous observation of the same spatial volume. This severely limits the utility of combing both image techniques as all dynamical information is lost.
Here, we discuss approaches and tools to minimize the mechanical and thermal noise, which are the major culprits hindering simultaneous spatiotemporal data acquisition with AFM and fluorescence microscopy. We have successfully circumvented existing problems and demonstrated simultaneous operation of aperture correlation microscopy through a Differential Spinning Disk (DSD) approach and nanomechanical mapping AFM [2,3]. We present the integration of a DSD imaging platform and an advanced bioscience AFM system capable of Quantitative Imaging (QI). This platform enables the collection of registered optical sectioning fluorescence and nano-mechanical mapping information of U2Os cells. The DSD illumination light fluctuates at time-scales much faster than the AFM cantilever movement providing a near-constant AFM cantilever illumination. Depending on the cantilever under consideration, this has the potential to avoid involuntarily induced cantilever bending by the fluorescence excitation light, which is an important problem when integrating far field fluorescence microscopy techniques with AFM.

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Figures

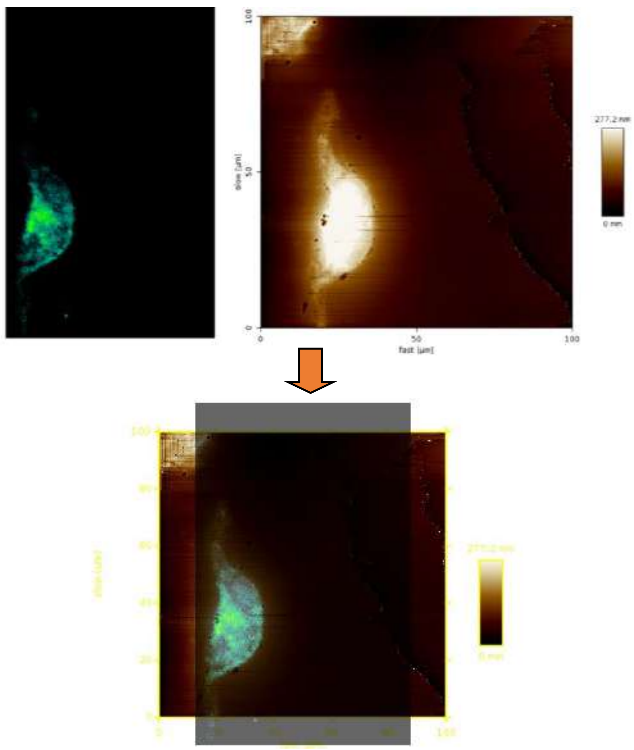

Figure 1: A fluorescence optical sectioned image and AFM QI™ height extended map and the corresponding image overlay of an U2Os cell labelled with GFP. For the AFM image we used triangular MSCT cantilevers. The scan was obtained over an area of 100x100 µm with 512x512 pixels.

Disclosing piezogeneration at the nanoscale with Direct Piezoelectric Force Microscopy

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Abstract
In this work I will present the new advances in the Atomic Force Microscopy (AFM) mode introduced in 2017 which enables researchers to map the piezogenerated charge with an Atomic Force Microscopy[1]. Until that date, the only method available to study piezoelectricity and ferroelectricity was Piezoresponse Force Microscopy. Despite the efforts this last decade, it is assumed by scientific community that PFM cannot be considered a quantitative technique [2]. The new mode aims to complement PFM, offering true quantitative data acquisition by collecting the current generated when a tiny force is applied to the material. A special transimpedance amplifier, with ultra-low level of leakage current is used in order to collect such amount of piezogenerated current.
In the talk I will introduce not only the mode itself, which was originally tested in three different piezoelectric materials, but the new advances there in. The speed of data acquisition has now been improved from 3 hours for a full images, to less than 10 minutes. Moreover, I will introduce some new measurements carry out in our facility that enables the use of the mode with a lockin amplifier, boosting the signal to noise ration of the measurements.

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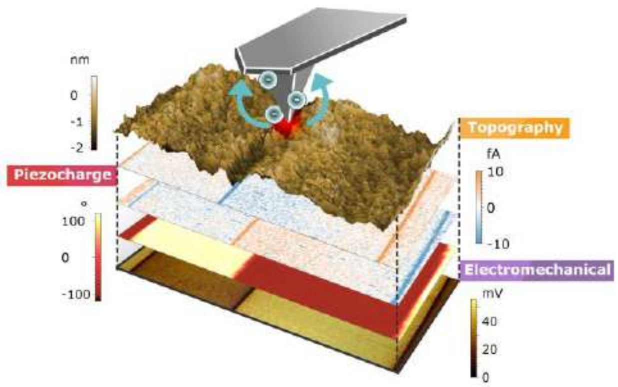

Figure 1: 3D rendered image obtained with the full information acquisition: both electromechanical and piezogeneration at the nanoscale are acquired with this new AFM mode.

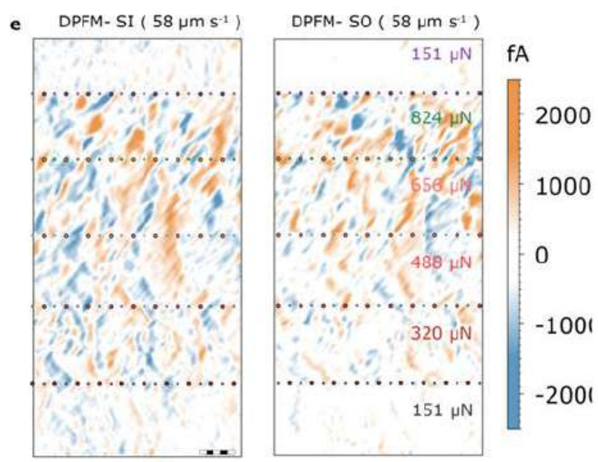

Figure 2: DPFM-Si and DPFM-So of a PZT sample acquired by performing DPFM. The images are obtained after a thermal treatment to grown the natural domains structure into the material to study

Humidity can induce phase transitions of surfactants embedded in latex coatings which can drastically decrease their performance

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Latex coatings are environmentally friendly i.e., they are formed from aqueous polymer dispersions, cheap to produce and provide exceptional mechanical properties. Therefore, they are ubiquitous and can be found in a wide range of different applications such as paints and varnishes, pressure-sensitive adhesives, textiles, construction materials, paper coatings and inks. However, they also have weaknesses and their surfactant content is among them [1]. Surfactants are often needed to stabilize polymer particles in the aqueous latex dispersions. These surfactants are also incorporated in coatings formed from these dispersions, and it is well-known that they can lower their performance. This work further explores this aspect and focuses on the role that embedded surfactant domains play in the response of latex coatings to humid environments. For this purpose, we made use of several experimental techniques where humidity control was implemented: quartz crystal microbalance with dissipation, atomic force microscopy and differential scanning calorimetry. By means of this multi-methodological approach we report that surfactants embedded in latex coatings can undergo humidity-induced transitions towards more hydrated and softer phases, and that this results in a drastic decrease of the mechanical and water barrier properties of the whole coatings (Fig. 1). Subsequently, this work highlights the potential of taking into account the phase behaviour of surfactants when choosing which ones to use in the synthesis of latex dispersions as this would help in predicting their performance under different environmental conditions.

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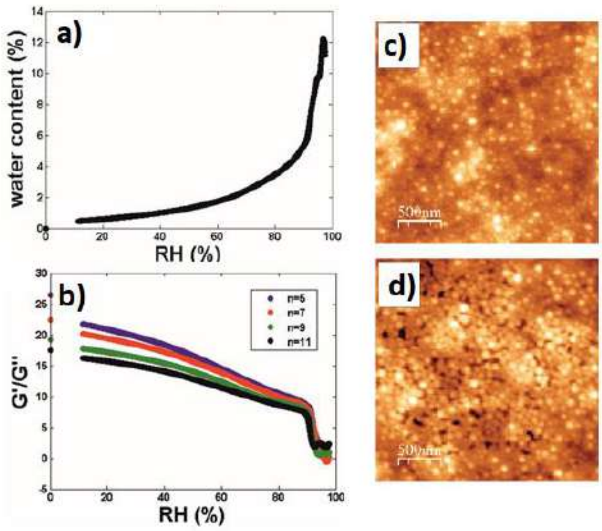

Figure 1: a) Water content and b) G'/G'' values as determined by means of QCM-D for a model latex coating. c) and d) AFM topographies of the same latex coating at 0% RH and 98% RH respectively. AFM images indicate the appearance of holes at high RH corresponding to domains of softer components (surfactants), responsible for the changes in water sorption and mechanical properties at high RH indicated by QCM-D.

Controlling photoacoustics enhancement with DNA nanostructures

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Molecular processes that occur on the nanometer scale can be studied using fluorescence molecular rulers based on the Förster resonance energy transfer (FRET) mechanism.[1] One important limitation of these fluorescent pairs is that their use in biological samples is limited to shallow imaging depths due to the light scattering.[2] The use of photoacoustic tomography (PAT)- a recently emerged high resolution modality for in vivo imaging that that combines optical excitation with ultrasound detection- represents an interesting approach to study such processes at centimeter depths.[3] However the capability to produce controlled distance dependent PA signal has not yet been proved.

In order to investigate this, we have exploited the capabilities provided by DNA nanotechnology to fabricate several DNA helices containing fluorophore-quencher pairs located over a range of different controlled distances. We have shown that PAT of the DNA helices showed distance-dependent PA signal generation (see figure 1) and experimentally demonstrated the potential use of PAT to reveal deep FRET processes within tissue mimicking phantoms.[4]

We have also demonstrated that DNA nanostructures are unique nanomaterials to augment the intrinsic PA signal of small molecule fluorescent Near Infrared (NIR) dyes.[4] This property together with their biocompatibility make them very promising contrast agent nanocarriers for cancer biomaging using PAT.

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Figure

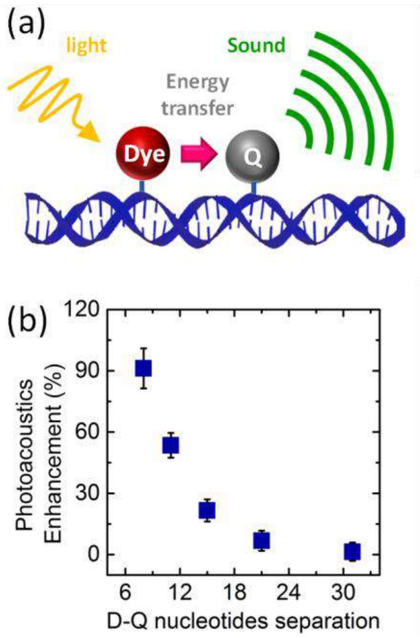

Figure 1: (a) Scheme and (b) graph showing the enhancement of PA signal as the distance between a dye and a quencher attached to a DNA helix platform is reduced.

NoCanTher: Nanomedicine Upscaling for Early Clinical Phases of Multimodal Cancer Therapy

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BIOPRAXIS faces drug development for rare cancers, including glioma and pancreatic cancer, using nanotechnology and biological molecules like proteins and peptides. Moreover, is also working in controlled release systems through nanoparticles, which improve therapeutic action of APIS and allow protection of biological molecules and targeting. BIOPRAXIS and some European Entities have worked previously in this area in protects as THERAGLIO project (Contract n FP-602923), MULTIFUN a finished FP7 project and HEATDELIVER: Heat and and Drug Delivery nanosystem with active tumortargeting features (Eurotransbio project). Based on the knowledge obtained, project NoCanTher (H2020-685795) aims at translating one of these nanoformulations to early clinical development for pancreatic cancer. The therapy is based on the functionalization of iron oxide nanoparticles using a targeting peptide and anti-cancer drugs, together with the effect of hyperthermia generated by an external alternate magnetic field. To successfully reach this objective, we will concentrate our efforts in two main group of activities:

• Nanomedicine up-scaling under GMP conditions: NoCanTher will scale up the manufacturing of the proposed nanoformulation from milligram-scale laboratory synthesis up to multigram-scale production to generate sufficient material for clinical and regulatory assays. To this aim, a GMP production line will be optimised and the relevant quality control will be conducted at the different stages of the up-scaling process.

• Clinical trial: NoCanTher will include late preclinical parameter testing to raise a clinical treatment protocol, regulatory assays, as well as the design of the clinical trial and the preparation of the Investigational Medicinal Product Dossier (IMPD). This strategy will allow us to apply for Clinical Trial Authorisation (CTA) then, we will carry out a Phase I clinical trial. NoCanTher involves the participation of institutions from three different sectors (academia, industry, clinical) and from five different countries (Ireland, France, Germany, Spain and the UK).

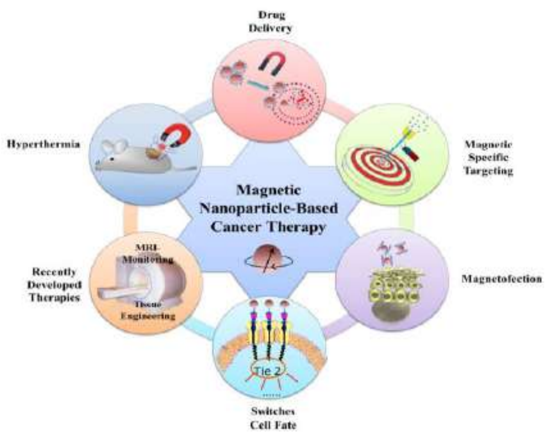

Figure1. Illustrating the process.

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Second-Principles Density Functional Theory: A systematically improvable multi-scale method including electrons and lattice degrees of freedom

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During the last two decades first-principles methods, particularly Density Functional Theory (DFT), have become an indispensable tool in the study of solid-state systems. However, interpreting or predicting the results of experiments requires, in many cases, to go beyond the length and/or time scales allowed by current computational power. Based on the idea that not all electrons play a relevant role in the determination of the physical magnitudes under scrutiny, we present a non-empirical, systematically improvable approximation to DFT based on a rigorous separation of these active electrons and holes from those of a reference electron density [1]. Using a similar expansion to that found in Tight-binding DFT methods we obtain a large term containing the energy of the reference system, and a second, much smaller one, associated to the active part of the electron density. By employing a well-tested model Hamiltonian to reproduce the energy surface associated to the reference system and representing the active electrons with a small but accurate Wannier function basis-set we obtain an efficient simulation method that can be used to calculate systems with tens of thousands of atoms with approximations that are systematically improvable towards DFT-quality. This method has been implemented in the SCALE-UP code (http://secondprinciples.unican.es; twitter @2nd_Principles). We provide several examples of its application in complex oxides including magnetism, metallic states and ferroelectricity [2,3].

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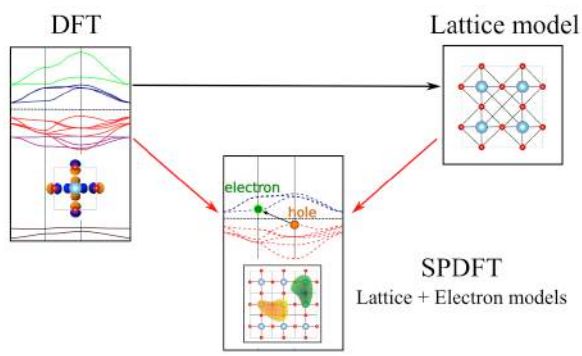

Figure 1: Illustration of second-principles density functional theory with respect to other related simulation methods

Monitoring Electrochemical Processes in a Safe Environment – from Metal Layers to Batteries

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For over two decades, scanning probe microscopy (SPM) has provided scientists a unique tool to study *in situ* electrochemical (EC) processes with atomic/molecular resolution. Nowadays, with the boom in alternative power sources using batteries, and the increase of interest in corrosion of lighter, thinner and more complex layer materials, surface studies under electrochemical potential control have found a new revival. New discoveries continue to be reported as the research boundary expands wider and deeper. While the field steadily advances, the requirements for electrochemical scanning probe microscopes also become greater.

Experiments under controlled environment have been considered critical for many surface studies – if you just think of lithium-based batteries, highlighting the oxygen-elimination capability of a standard environmental chamber. This is one of the main prerequisites for successfully studying structural changes during charging/discharging processes, or any morphological changes during electrochemically controlled processes.

Examples presented range from studies of metallic and molecular layers under electrochemical and environmental control (temperature, solvent, atmosphere), electro-polymerization of poly-electrolytes using cyclic voltammetry, up to studies of "real-world" samples like corrosion studies on steel alloys or applications in non-aqueous battery technology (lithium- and tin-based substrates [1] or graphite [2]), see figure 1.

In summary, several techniques and examples will be shown that demonstrate the capabilities of electrochemical SPM for topographical imaging on the nanometer scale and simultaneously modifying a surface under potentiostatic and environmental control.

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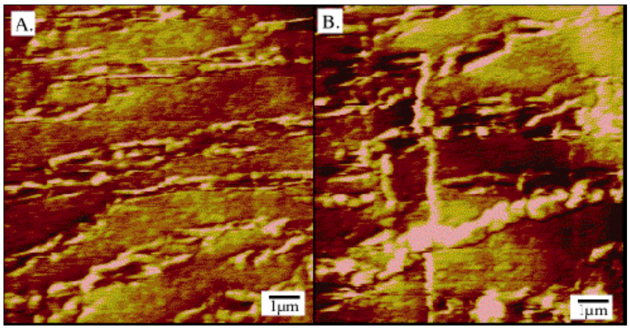

Figure 1: Illustrating morphological changes on a lithium film in non-aqueous electrolyte.
(A) 10μm topography image of a proprietary lithium foil in electrolyte solution.
(B) The same area after 40 consecutive potential sweeps mimicking charging/ discharging processes, where several cracks in the surface become apparent.

Nano/Microbilayer Hemostatic Agents in Diabetic Injury Wound Model in Rat

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Diabetes mellitus (DM) is a chronic, life-long metabolic disease, which is associated with nephropathy, retinopathy, and neuropathy for microvascular systems and coronary artery disease and strokes and peripheral arterial disease for macrovascular.[1-3] In besides hypercoagulability and hypofibrinolysis, the wound complication problems in surgical patients with diabetes mellitus is a serious problem in clinical practice. Therefore, effective bleeding control for a person with diabetes is more essential compared to a healthy person in military and civilian life. For this purpose, we prepared a nano/microbilayer hemostatic dressing that has a porous sublayer, including chitosan (CTS), bacterial cellulose (BC) as basement and active agents in coagulation cascade, such as vitamin K (Vit K), protamine sulfate (PS), and kaolin (Kao) as a filler and an upper layer consisting of silk fibroin (SF) or SF/phosphatidylcholine (PC) blend to achieve complete hemostasis in diabetic rats. Coagulative performances of the prepared hemostatic dressings were examined by the determination of bleeding time, blood loss, and mortality rate through diabetic rat femoral artery injury model. According to the obtained results, Vit K-reinforced within 138 s and SF-coated BC/CTS hemostatic dressings within 144 s showed a rapid coagulation time.

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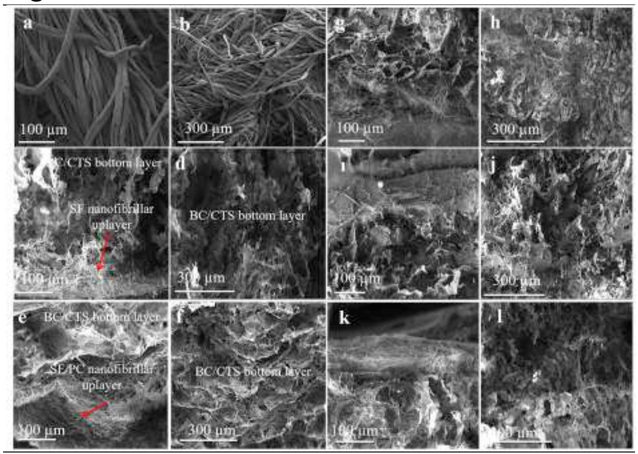

Figure 1: (a, b) SEM micrograph of standard gauze and cross-sectional SEM micrographs of (c, d) SF-coated BC/CTS, (e, f) SF/PC-coated BC/CTS, (g, h) SF-coated Kao/BC/CTS, (i, j) Vit K/BC/CTS, and (k, l) PS/BC/CTS hemostatic dressings (left images: bilayer structures, scale bars:100 mm; right images: sub-porous structures, scale bars: 300 mm).

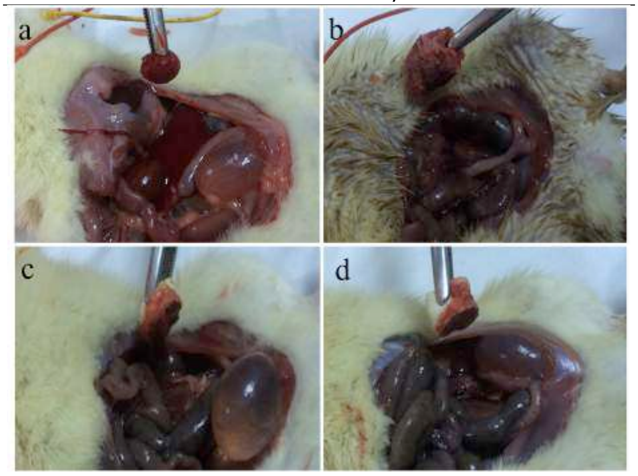

Figure 2: Bleeding site after application in a diabetic rat femoral artery model: (a) standard gauze, (b) SF-coated BC/CTS, (c) SF-coated Vit K/BC/CTS, and (d) SF-coated PS/BC/CTS.

Chiral gold nano-hooks for increased LSPR sensitivity

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Plasmonic nanoparticles (NP) with their localised electron oscillations (localised surface plasmon resonance, LSPR) constitute a common tool for sensitive refractive index sensors [1]. A new approach using chiral NPs in combination with circular dichroism (CD) spectroscopy shows promising results for increasing the sensitivity of this method.
In contrast to the standard fabrication method of chiral NPs which utilizes layered electron-beam lithography [2] the present hooks are fabricated using a faster and cheaper bottom-up approach called hole-mask colloidal lithography (HMCL) [3].
HMCL is based on the self-assembly of charged nano-spheres on a sacrificial layer for the creation of a hole-mask. Here I report how this hole-mask can be combined with glancing-angled physical vapour deposition (GLAD-PVD) for achieving a simple way of making chiral NPs. Crucial to this novel method is the exploitation of the clogging of the hole-mask during deposition [4]. When depositing material while simultaneously tilting and rotating the sample this clogging straightforwardly leads to the formation of the here presented nano-hooks.
Measuring the spectral absorbance of these Au nano-hooks (see fig. 1) reveal multiple plasmonic responses that correspond well to previous results for other Au NPs [1]. Furthermore, CD absorbance measurements show differential shifts of the resonance peaks when comparing the two handedness of circular polarization. These shifts appear to be more sensitive to the surrounding refractive index than the standard (unpolarized) spectroscopic approach.
Therefore, these novel NPs are a promising instruments for improved sensitivity of LSPR-biosensors, with high sensitivity and a cost- and time-efficient fabrication method.

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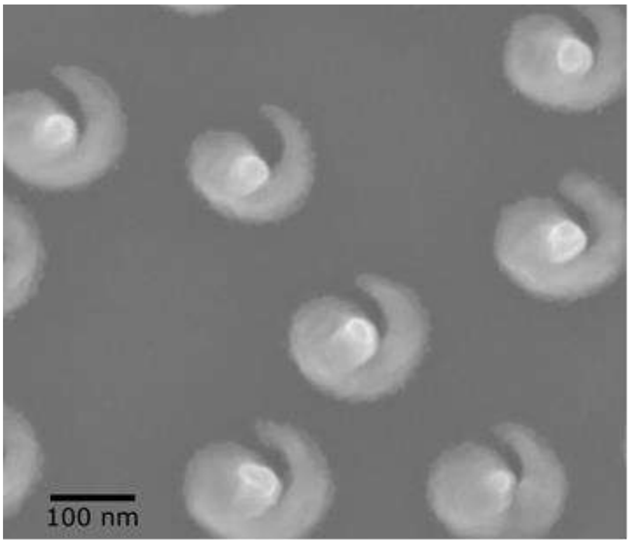

Figure 1: Scanning electron microscope image of chiral gold nano-hooks.

Laser-reduced graphene for energy storage devices

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Graphene has attracted increasing attention in recent years [1] due to its excellent mechanical, optical and electrical properties. Its high theoretical surface area (2630 m2/g) and high electrical conductivity make it an attractive material for many industrial applications [2].
A layer of graphene can be prepared by several techniques: mechanical exfoliation from graphite, sublimation on a silicon carbide surface, or chemical vapor deposition growth on Cu or Ni. All these techniques produce high quality graphene, but may be quite expensive for industrial applications. Alternatively, the reduction of graphene oxide (GO) is a low cost technique for obtaining graphene material.

We report the reduction of GO by using an infrared laser. This is a single-step and scalable procedure which allows to make circuits and complex designs on different substrates without the need for chemicals, masks, catalysts or expensive equipment [3, 4]. Furthermore, the reduction degree of the oxide and, consequently, its electrical properties can be controlled by varying the laser intensity and the number of times that GO is exposed to the procedure.

The material obtained by this reduction process proves to be mechanically robust, with a high electrical conductivity and a high specific surface area. Therefore, this laser-reduced graphene oxide is an outstanding material for high-performance electrochemical capacitors as we also report in this work [5, 6].

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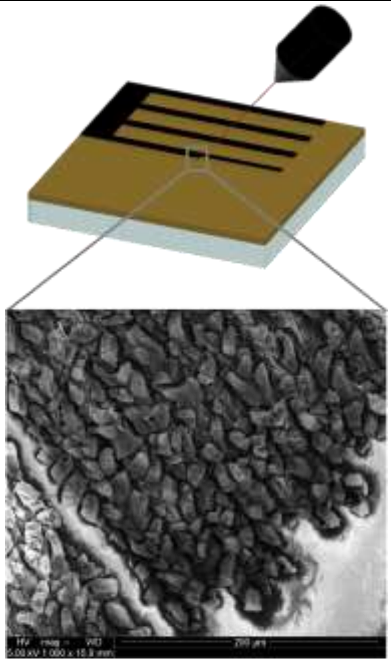

Figure 1: Schematic illustration of the reduction process and SEM picture of the laser-reduced GO.

Acknowledgements

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Detecting Mechanochemical Atropisomerization within an STM Breakjunction using Porphyrins

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Abstract

The study of porphyrin molecular wires is a fruitful area within the field of molecular electronics [1, 2, 3]. We have employed the scanning tunneling microscope break-junction technique to investigate the single-molecule conductance of a family of 5,15-diaryl porphyrins bearing thioacetyl (SAc) or methylsulfide (SMe) binding groups at the *ortho* position of the phenyl rings [1]. These *ortho* substituents lead to two atropisomers, *cis* and *trans*, for each compound, which do not interconvert in solution under ambient conditions; even at 140 °C, isomerization takes several hours ($\Delta H^‡$ = 63 kJ mol^{-1}; $\Delta S^‡$ = – 200 J mol^{-1} K^{-1} for SAc in $C_2Cl_4D_2$). They can be separated quite easily allowing us to study the single molecule conductance behaviour of *cis* and *trans* isomers independently. During elongation of single molecule junctions at room temperature, isomerization does in fact take place when the binding group is SAc, but not SMe, due to the strength of the Au-S bond. When the binding group is SMe, the difference in junction length distributions between *cis* and *trans* isomers reflects the difference in S-S distance (0.3 nm) between the two. In the case of SAc, we find no discernible differences between the plateau length histograms of the two isomers, and both show maximal stretching distances well exceeding their calculated junction lengths. Contact deformation accounts for part of the extra length, but the results strongly suggest that *cis*-to-*trans* conversion takes place in the junction for the *cis* isomer. The barrier to atropisomerization is lower than the strength of the thiolate Au-S and Au-Au bonds, but higher than that of the Au-SMe bond, which explains why the strain in the junction only induces isomerization in the SAc compound. This implies that the porphyrin ring adopts significantly non-planar conformations within the junction.

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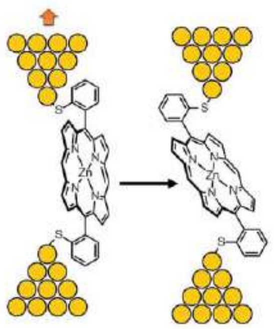

Figure 1: Mechanically-induced atropisomerization in a single porphyrin molecular junction.

Ag-ZrO2 cermet coatings sprayed onto steel sheet

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Abstract

A new pathway is proposed to produce solar selective cermet coatings on the base of silver nanoparticles embedded in amorphous zirconia deposited onto aluminized steel sheet (AS) by chemical spray pyrolysis. We show that silver nanoparticles can be obtained by a simple and cheap air pressure spray technique when using mixed (Ag + Zr) precursor solutions. Silver particles are metallic as shown in an XPS study [1]. Here various Ag-ZrO_2 multilayer coating systems were studied with respect to their solar selective properties (UV-VIS-IR) in relation to layer structure (SEM/FIB; TEM/EDS) and silver nanoparticle size distribution (AFM).

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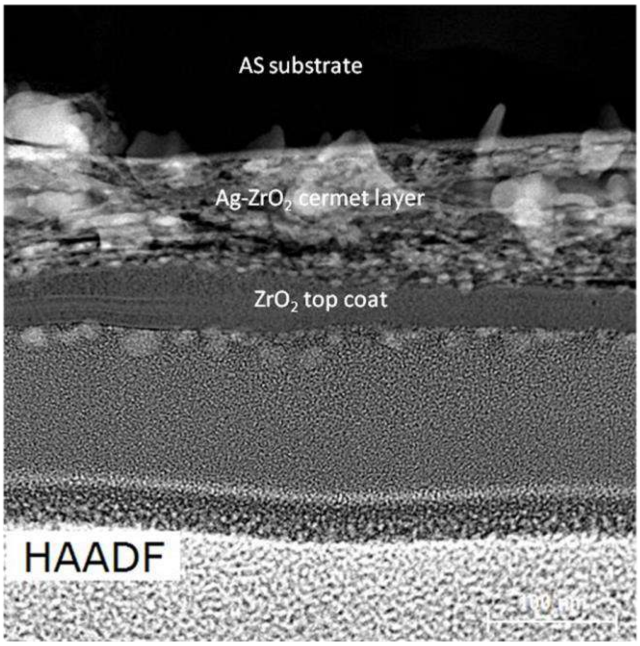

Figure 1: HAADF-STEM image of the lamella cross section of sample ZrO_2/Ag+ZrO_2/AS

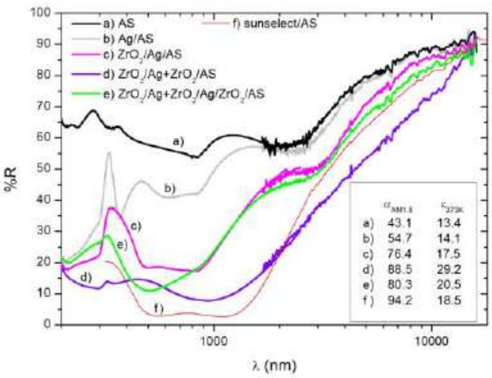

Figure 2: Total hemispherical spectral reflectance of the coatings in comparison to the aluminized steel substrate (AS). Solar absorptance for AM1.5 and thermal emittance at 373 K of the coatings and the substrate are indicated in the inset.

Measuring and controlling out-of-plane shape of free-standing 2D materials

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In this work, we show through transmission electron microscope (TEM) and atomistic simulations that the non-flatness of free-standing graphene, hBN, and MoS_2, as well as their heterostructures varies depending on the material. Out of all studied materials, graphene is the least flat, followed by hBN and finally MoS_2. For the heterostructures, the overall shape is determined to a large extent by the stiffer of the two materials.

In addition to measuring the out-of-plane shape, we can also control it *in situ* in one direction using a stretching holder. For these experiments, we glued the samples, transferred onto gold TEM grids with a perforated amorphous carbon film, onto the holder and applied mechanical strain with small incremental steps to avoid breaking the film during the experiment. Figure 1 shows the results of one such study. The deviation of circular symmetry of the diffraction pattern and the shape of the individual diffraction spots give us insight on the strain in the material and its out-of-plane shape, respectively.

Our results show that this simple method can be used to completely flatten the 2D materials in the direction of the applied force. At this point, the material exhibits an aligned set of one-dimensional corrugations. After the structure has been flattened, continuous mechanical deformation leads to a measurable strain in the structure.

Figures

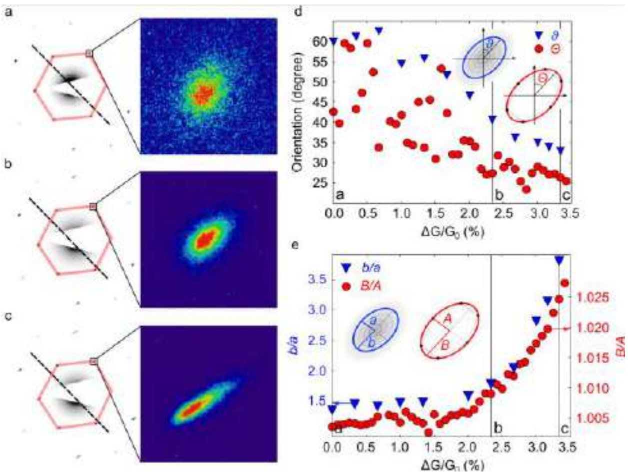

Figure 1: Evolution of the diffraction pattern of graphene and individual diffraction spots during the experiment. (a-c) Diffraction pattern recorded at different stages of the experiment: (a) at the beginning, (b) towards the end and (c) at the end. All shown patterns were recorded at sample tilt a = 21°. The dashed lines show the approximate tilt axis and the overlaid hexagons highlight the first set of diffraction peaks. The panels on the right show a zoom-in of the indicated diffraction spots in false color. (d) Orientation of the ellipse fitted to the diffraction patterns (Θ) and that of the diffraction spots (θ) during the experiment. (e) Ellipticity of the diffraction patterns (B/A, right y-axis) and spots (b/a, left y-axis). Standard errors from the fits to the measured values are contained within the markers. All diffraction pattern values are for a = 0° and spot values for a = 21°. In panels d and e, the values corresponding to the diffraction patterns shown in panels a-c are marked with corresponding labels. The x-axis values ($\Delta G/G_0$) indicate the relative change in the size of the gap in the sample carrier over which the sample was suspended.

Surfactant-free β-galactosidase micromotors for "on-the-move" lactose hydrolysis

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Lactose is the most abundant disaccharide in milk and essential for the nourishment of newborn infants. Lack of the enzyme lactase in the small intestine resulted in heavy digestions and stomachache. Enzymatic hydrolysis using the enzyme β-galactosidase has proven to be a convenient way to broke lactose into glucose and galactose, which can be easily absorbed by the intestinal tract, avoiding such milk intolerance. Biocatalysts immobilization onto nanosupports possess several advantages over traditional chemical technologies such as higher specificity, facile product separation and the possibility to work in continuous operation. Herein we describe the use of surfactant-free carbon nanomaterial catalytic micromotors as moving nanosupports for the immobilization of β-galactosidase towards highly efficient lactose hydrolysis in continuous mode.
Self-propelled micromotors hold considerable promise as "dynamic supports" for the immobilization of enzymes for a myriad of applications. Indeed, micromotors presents several advantages compared to traditional materials employed in immobilized biocatalysts due to their capability to move in the reaction media eliminating substrate diffusion necessity. The concept is illustrated in Figure 1. The micromotors are prepared by template electrodeposition using multiwalled carbon nanotubes (MW) as outer layer for further functionalization and Ni-PtNPs for inner layer that allows efficient self-propulsion in milk an easy recovery from sample by magnetic separation. Enzyme β-galactosidase is immobilized by covalent chemistry leading to functional structure with potential to eliminate lactose in raw milk samples. The micromotors can propel in skimmed milk without the aid of any surfactant, opening new avenues for its application in food applications. The immobilized β-galactosidase activity and stability are evaluated under different temperature and pH conditions. Immobilized biocatalyst micromotors reusability by magnetic separation from sample and their performance in real skimmed milk are studied towards efficient operation in food industry.[1]

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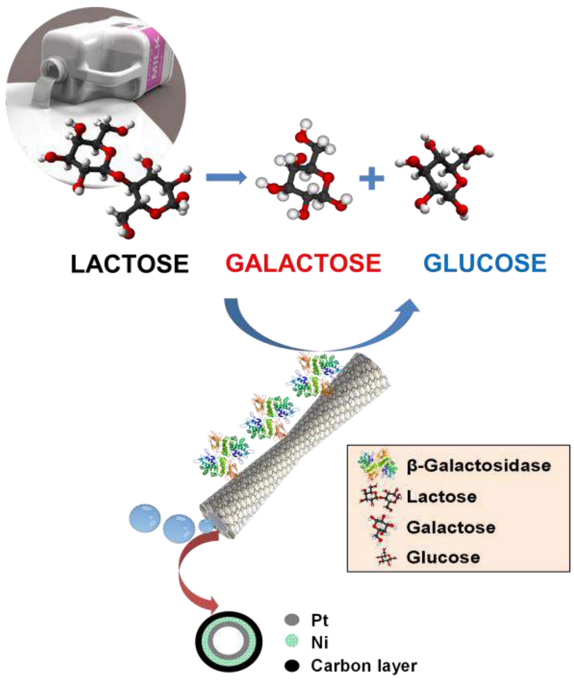

Figure 1: Surfactant free β-galactosidase micromotors for lactose removal from milk.

Simulation of nanoscale AlGaN/GaN high -electron mobility transistors employing field-plate structure

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Abstract

Wide band-gap and high breakdown electric field allows high terminal voltage operation of the transistor based on Gallium nitride technology. The excellent microwave power performance demonstrated in AlGaN/GaN HEMTs (high-electron mobility transistors) results from the combination of high current density with high voltage operation [1], which benefits from the high sheet charge density in these hetero-structures (1013 cm-2), the high carrier mobility (1500 cm2/Vs) and saturation velocity (1.5 × 107 cm/s) in the channel and the high breakdown voltage inherent in the GaN material. However, their reliability still limits their applications in today's electronic systems. The newly developed field-plated AlGaN/GaN high electron mobility transistors show improved performance due to the electric field reduction in the device channel and surface modification [2]. We report on two dimensional numerical simulations of gate-recessed and field-plated AlGaN/GaN HEMTs where all the important device parameters have been defined, the insulator thickness under the field plate is also an important design parameter to attain higher breakdown voltage, thus an improvement of the performances of HEMT devices.

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Use of biological nanoparticles for degradation of Non degradable polymers

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Abstract

Petroleum based polymers have become an indispensable part in every area of human life. They are chemically inert and resistant to microbial attack. Due to its recalcitrant nature its has emerged as a potent pollutant with hazardous effects due to poor waste disposal and degradation management. Microbial degradation of these plomers will provide of non chemical, eco friendly, low cost technology application which will help in plastic waste management. Various researchers have shown that these ploymers are prone to degradation due to effect of biotic and abiotic factors. The biotic factors mainly includes the microbial system in which they are exposed. Studies have shown that nanoparticles have unique ability in enhancement of polymer degradation. Nano particles help in augmentation of biodegradation rate by having a positive impact on the growth profile of microorganisms. Various fungi and bacterial species has been reported for their biosynthetic ability to synthesize silver, gold and platinum naoparticles. This review article primarily focuses on the imapct of biological nanoparticles on the degradation of synthetic, petroleum based polymers.

Device design parameters for carbon nanotube field-effect transistors

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Abstract

Among the extraordinary electrical characteristics, such as low scattering rate and high current-carrying capability, the intrinsic linearity of carbon nanotube (CNT) field effect transistors (CNTFETs) is expected to be beneficial for future high-frequency (HF) applications once the device is optimized [1], [2]. Performance projection studies [3] and fabricated proof-of-concept HF circuits [4]-[6] have shown the feasibility of CNTFETs for HF applications. Some technology related issues can be overcome by sophisticated techniques [7] and an adequate device characterization [8]. However, modeling and technology groups efforts are developed towards an optimized device suitable for mass production. An important performance parameter of the transport properties of the channel, such as the mobility, helps the device optimization. In addition, the metal-CNT interfaces, key factors limiting the device performance, need to be properly characterized by a Schottky barrier and a contact resistance in order to improve the current injection [9], [10]. A review on concepts and extraction methods of Schottky barrier height, contact resistance and mobility for carbon nanotube field-effect transistors (CNTFETs) is presented. The methods are applied to synthetic and experimental data of single- and multi-tube CNTFETs with short- and long-channel lengths obtained by our group [8], [11], [12].

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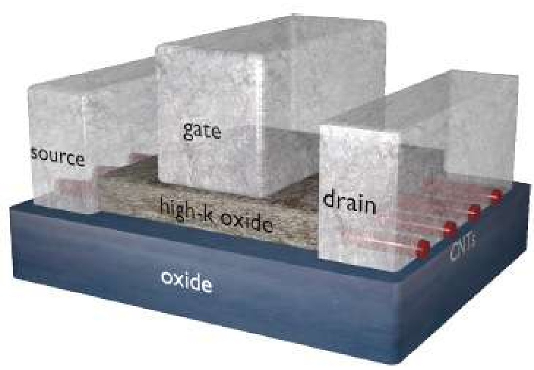

Figure 1: Top gate multitube CNTFET

Silica nanoparticles for bioimaging and Photodynamic Therapy

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Abstract

Mesoporous silica nanoparticles are potential drug delivery systems for biomedical applications. Spherical nanoparticles are synthesized by Stöber method with core-shell structure and monodisperse size distribution of around 50 nm, Figure1.[1] In this work, fluorescent dyes are embedded in the core and photosensitizers (PS), able to generate singlet oxygen (cytotoxic species), are grafted on the shell to trigger dual activity bioimaging and photodynamic therapy respectively.[2]
The hybrid system has been optimized with commercial photosensitizer; Rose Bengal (RB) or Thionine (Th) before using new photosensitizers based on BODIPY structure.
To improve stability in water for biological applications a short chain of polyethylene glycol (PEG) is anchored to the external surface, Figure 2. Moreover, PEG prolongs the hybrids system life-time in blood.[3] As a result, well-dispersed silica nanoparticles with good singlet oxygen production and well-dispersed are obtained. "In vitro" experiments will be carried out to check their phototherapy activity in Hela cells.

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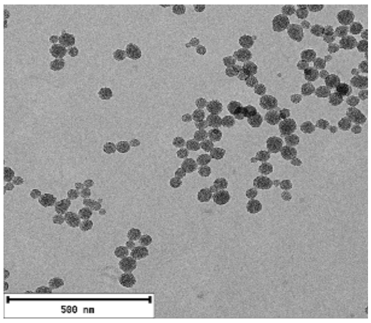

Figure 1: TEM image of mesoporous silica nanoparticles with around 50 nm size

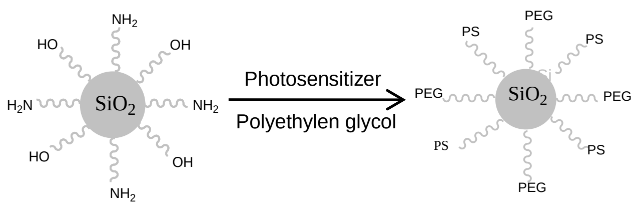

Figure 2: Schematic representation of nanoparticle grafting

Designing and reading magnetic lateral flow strips for point-of-use food and clinical applications

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Point-of-care devices are desired for multiple bio-applications ranging from medical screenings in the health centre, urgent diagnosis by the first responders to in situ industrial bio-analysis (point-of-use). The primary needs to accomplish are portability, rapidity, and low cost.
Lateral flow immunoassays (LFI) in nitrocellulose strips meet those conditions and can be made quantitative and precise if the goal bio-analyte is labelled by magnetic nanoparticles. In this work we report magnetic LFI for histamine detection in liquids and a portable reader [1] to quantify in the range of interest for wine tests.
Histamine is produced during the fermentation process of wine (and other food products) [2,3]. The ingestion of histamine above certain levels may cause serious toxicological problems. For this reason, it is very interesting to set a rapid and inexpensive method for the detection and quantification of histamine in wineries.
Figure 1 schematises the development of the test in competitive format: (a) The sample containing histamine is mixed up with anti-histamine antibody and deposited at one end of the nitrocellulose strip, along which it flows by capillarity; (b) The free antibodies in the sample occupy sites in the test line; (c) Protein G-nanoparticle conjugates get attached to the antibodies in the test line, providing a signal which is inversely proportional to the amount of histamine in the original sample; (d) LFI strips for different concentration of histamine (increasing from left to right).

These magnetic tests can be also applied in the clinical field as diagnostic tool. With this purpose, sandwich immunoassays at the tests strips have been developed for detection of Prostate Specific Antigen (biomarker of prostate cancer) and troponine (biomarker of cardiac diseases). The magnetic sensor developed in this work was applied for quantification.

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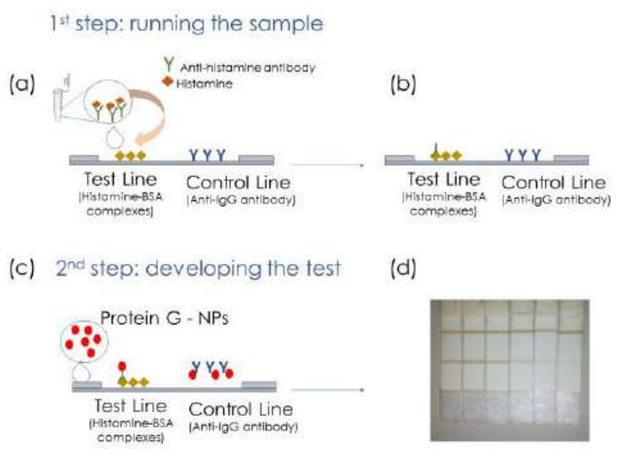

Figure 1: Competitive lateral flow immunoassay (LFI) for histamine detection.

Sol-Gel Microencapsulation Of $NaNO_3$ As Phase Change Material For Thermal Energy Storage

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Abstract

$NaNO_3$ has been selected as Phase Change Material (PCM) due to its convenient melting and crystallization temperatures for Thermal Energy Storage (TES) in solar plants or recovering of waste heat in industrial processes [1,2]. However, incorporation of $NaNO_3$ requires its protection (i.e. encapsulation) into containers or support materials to avoid incompatibility or chemical reaction with the media where incorporated (i.e. corrosion in metal storage tanks). As a novelty, in this study, sol-gel microencapsulation of the inorganic salt has been carried out using also an inorganic compound (SiO_2) instead of the conventional polymeric shells used for organic microencapsulations and not suitable for high temperature applications (i.e. 300-500 °C) [3-4]. Feasibility of the synthetized microparticles has been demonstrated by different experimental techniques in terms of thermal energy storage capacity and thermal stability and durability through thermal cycles. The effectiveness of microencapsulated $NaNO_3$ as thermal energy storage material depends on the core:shell ratio used for the synthesis and on the maximum temperature supported by $NaNO_3$ during use.

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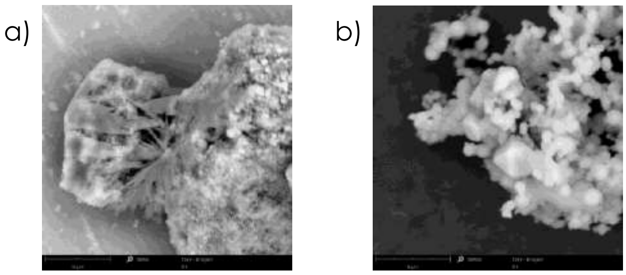

Figure 1: Micrograph by Scanning Electron Microscopy (SEM) of $NaNO_3$-SiO_2 microparticles with different core:shell ratio

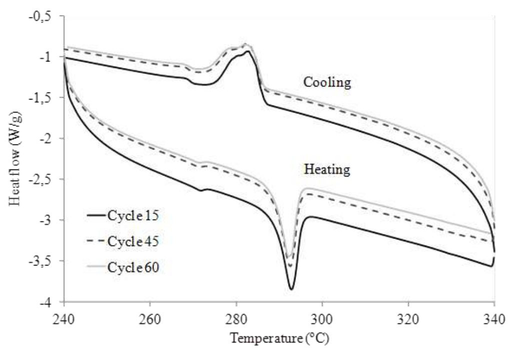

Figure 2: Thermograms by Differential Scanning Calorimetry (DSC) of $NaNO_3$-SiO_2 microparticles after thermal cycles

Acknowledgements

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Polyoxometalate-chitosan nanogels for breast cancer therapies

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Abstract

Tumour recurrence is one of the most serious limitations of current hormonal breast cancer treatment. Polyoxometalates (POMs) are anionic metal-oxo clusters that have recently shown to be capable of inhibiting signalling pathways in cancer stem cells *in vitro* [1], which is a key factor for resistance to estrogen mediated therapy. One of the main drawbacks of POMs as anticancer agents is their cytotoxicity and the difficulty to be incorporated into the cell. In order to improve both aspects it is necessary the development of nanocarriers which encapsulate them and ensure both the protection of the anticancer agent in healthy physiological environment, and the specific release inside tumour cells.
Chitosan nanogels constitute a good approach to stimuli-responsive nanodevices because of their unique properties: biocompatibility, biodegradability and pH-sensitive behaviour, as well as their structure of three-dimensional networks.
Chitosan is a biopolymer which behaves as a soluble cationic polyelectrolyte in acidic solutions due to the protonation of their glucosamine units. Consequently, chitosan networks swell at acidic pH, while remain collapsed at physiological pH.
Besides, it is well known that the pH of tumoral tissues is small but significantly lower than that of healthy ones[2]. Therefore, pH-sensitive gels have emerged as interesting drug nanocarriers [3]. This is the case of chitosan nanogels whose swelling at acidic pH would contribute to a high loading and specific POM release in tumoral sites, avoiding the damage in the surrounding healthy tissues.
Following this approach, Wells-Dawson type POMs $K_6[P_2Mo_{18}O_{62}]$ were successfully encapsulated into water dispersable chitosan-based nanogels. Nanoparticles were prepared by covalent crosslinking reaction of chitosan with poly(ethylene eglycol bis(carboxymethyl)et her), in reverse microemulsion medium. Loading efficiency of the POM was determined to be close to 90%. The release profile was also studied and a controlled release under different pH conditions was observed. Experimental results enhance the potential use of the prepared particles as nanobiomaterials for more effective therapies in the total eradication of breast tumours.

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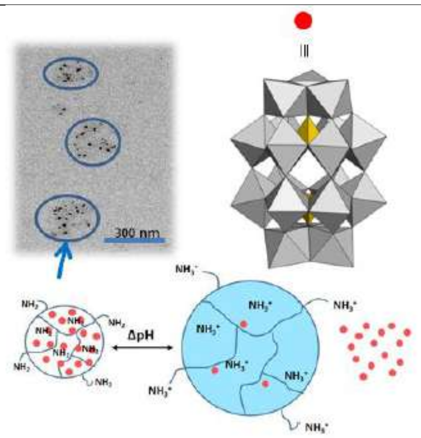

Figure 1: pH-sensitive POM release for chitosan nanogels.

3D magnetometry in ultrathin magnetite using XMCD-PEEM

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One of the main trends in the magnetism roadmap is the study of the magnetic configuration and magnetization dynamics of magnetic nanoelements [1]. Nanomagnets have indeed many potential applications including data storage systems, magnetic logic devices or biomedical applications. Size reduction has considerable advantages in terms of increasing the device density, but also there are new magnetic phenomena linked to the nanoscale. In most of the new devices and applications, the magnetic configuration of the nanoobjects plays a key role in the properties and the performance of the device. Different microscopy techniques like magnetic force microscopy can be used to explore the magnetic configuration of these nanoobjects. However, these techniques normally do not provide us with information about the 3D configuration of the magnetic moments, which could be crucial in many cases. In this work we use XMCD-PEEM for 3D magnetometry in micrometer wide and tens of nanometers thick in-situ grown single crystal islands of magnetite.

The experiments have been performed at the CIRCE beamline of the Alba synchrotron. The station comprises a preparation chamber and the main chamber that houses the low-energy electron microscope (LEEM) with energy analysis capabilities. The instrument, an Elmitec III microscope, can be used in low-energy electron mode to provide real-space observations of the growth front during molecular beam epitaxy. It can also provide low-energy electron diffraction (LEED) patterns of selected areas of the sample as small as a fraction of a micrometer. In photoemission mode (PEEM) and coupled to the Alba synchrotron, it provides selected area x-ray absorption spectroscopy without the need to transfer the sample after growth.

In this work we show how XMCD-PEEM, combined with imaging and data analysis, is a very powerful tool for the study of magnetic configurations of nanometer sized objects [2]. This technique allows 3D mapping of the magnetic moment together with the estimate of the orbital and spin contribution to the local magnetic moment as can be seen in figure 1.

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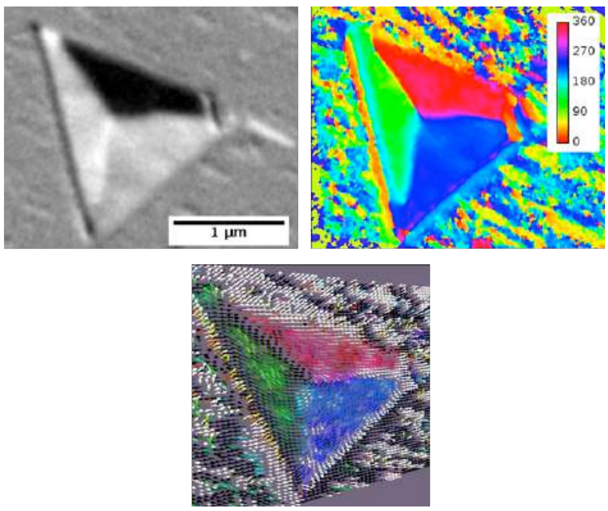

Figure 1: a) LEEM image of magnetite island. b) Magnetic domains measured by XMCD-PEEM. The color scale indicates the azimuthal angle of the magnetization vector. c) 3D magnetic image.

Interpretation and applicability of parallel superposition rheology techniques on liquid like flocculated hard sphere dispersions.

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Abstract

The use of superposition rheology for the study of microstructure behaviour on flowing dispersions was proposed several decades ago and early analysed by H.C. Booji [1]. Of the two main configurations (parallel and orthogonal superposition) orthogonal superposition is far more used because of its little interference with the flowing structure and, in consequence, its analytical simplicity. However, the parallel geometry rotatory rheometer is widely used in rheometric and colloidal laboratories. This work is an attempt of providing an analysis of the technique and a simple model for applying it and be able to interpret its results.

This work make use of the current knowledge of clusters and some previous work on this topic like good predictions of Dhont [2] emerged from his mathematical analysis. We attempt a prediction of the qualitative behavior of floc based micro-structure and its stability under a superposed oscillatory shear. An evaluation of the conditions of applicability is performed by relying on the interferences mathematically described on [3].

We focus on flocculated colloidal dispersions of hard spheres ligated mainly by double layer electronic repulsion and Van der Waals attraction. A liquid like phase is required for our model. Only structures ligated by the secondary minimum equilibrium point of the interaction potential are analyzed.

Given a stress model, simulations are performed showing parallelisms with external results of nonlinear shear tests like LAOS [4].

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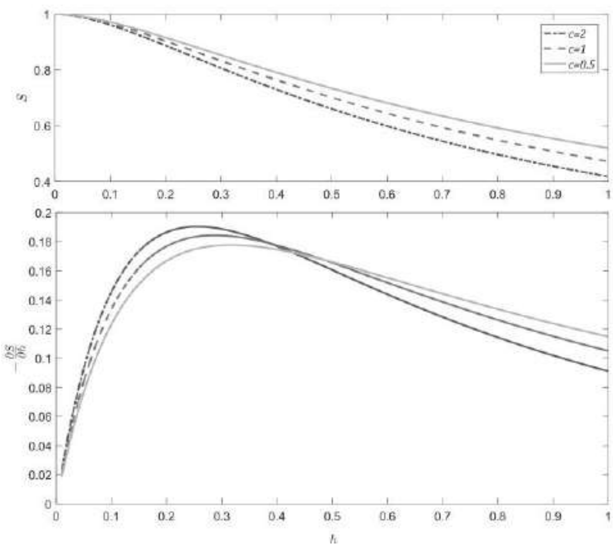

Figure 1: Adimensional structure potential (*S*) versus adimensional dispersion parameter (*h*).

Size-Effect on Superelasticity at Nano-scale in Shape Memory Alloys for Potential Applications in MEMS

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Shape Memory Alloys exhibit a superelastic stress-induced phase transformation with a high displacement actuation, which are promising for applications in Micro Electro-mechanical Systems (MEMS). Previous works demonstrate a completely reversible and reproducible behaviour at nanoscale [1,2], even for thousands of cycles [3]. However, some fundamental aspects at nanoscale remain unclear, in particular whether the critical stress for superelasticity exhibits a size-effect similar to that observed in confined plasticity. Our results provide the evidence of a strong size-effect on the critical stress that induce such phase transformation [4]. This has been observed in pillars, milled by FIB in single crystal slides from Cu-Al-Ni and other SMA, from 2 μm to 260 nm in diameter. The critical stress for superelasticity has been measured by nano-compression tests.
A power-law size dependence of n=-2 has been determined for the superelasticity at nanoscale. Our observations are explained through an atomistic model, involving the atomic lattice shearing triggered by the elastic strain during homogeneous martensitic transformation.

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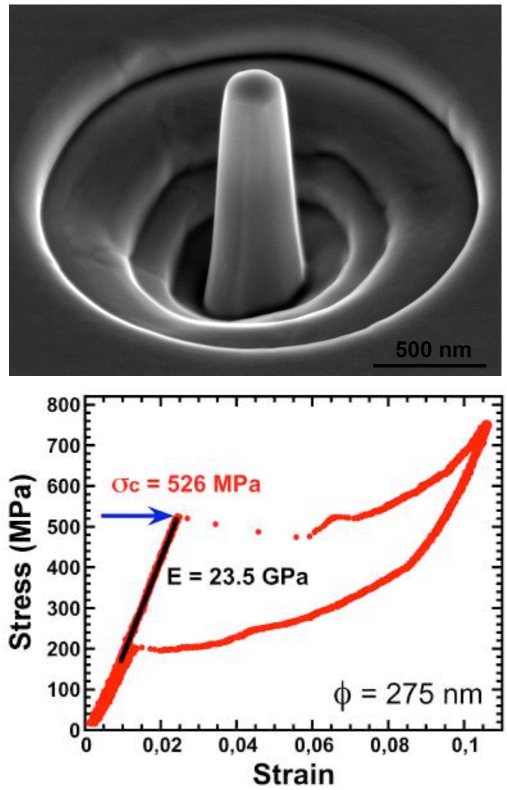

Figure 1: Cu-Al-Ni pillar, 275 nm in diameter, and the nano-compression superelastic test

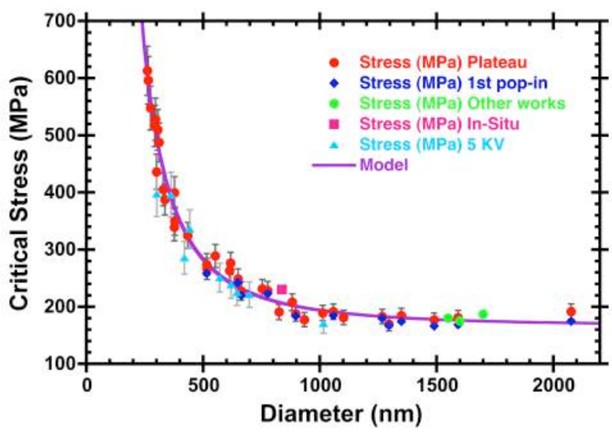

Figure 2: Size-effect measured on the critical stress for superelasticity, versus pillar diameter, and the prediction of the proposed model [4].

Tuning phonon thermal transport through graphene by using ensembles of molecular antiresonances

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We propose a scheme for engineering thermal transport properties of low dimensional materials. The method consists of three main ingredients. First, we introduce antiresonance lineshapes in phonon transmission spectrum by molecular functionalization. Even though different molecular species give rise to diverse transmission spectra, thermal resistances due to different species are quite similar, because of the bosonic character of phonons. The bosonic character gives rise to another important feature, which is the second ingredient of the proposed scheme. Combinations of series of phononic thermal resistances are not additive, in general. The more different the transmission spectra of individual scatterers are, the larger total thermal resistance becomes. The third ingredient of the scheme is optimization of the thermal conductance by constructing suitable combinations of scatterers. We use combinatorics principles to show that it is possible to obtain large variances in thermal resistance. We show that a wide range of thermal conductance values are possible, where the range to the average ratios as high as 0.66 are predicted at room temperature, while it can be as high as 1.46 at low temperatures. These figures demonstrate the tunability of thermal transport using the proposed scheme.

Figures

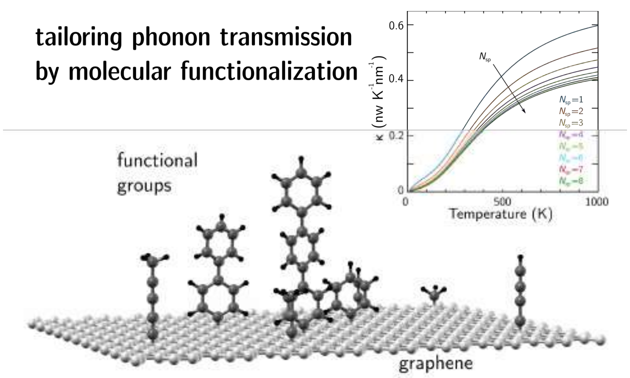

Figure 1: Tailoring phonon transport by chemical functionalization

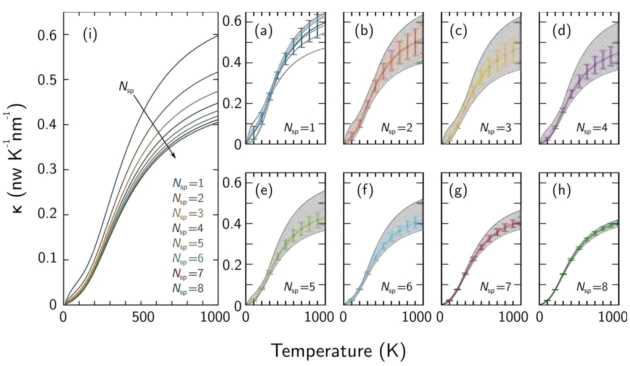

Figure 2: Thermal conductance for ensembles containing 100 molecular adsorbants distributed over different number of species, N_{sp}.

An innovative nanocarrier for neuroprotection

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In the last decades, the incidence of age-related neurodegenerative diseases (ARND) has gained relevance due to the progressive increase of average life expectancy and the limited therapeutic solutions available [1]. The multifactorial etiology of ARND suggests the benefit of investing in the study of multi-target active compounds, such as plant polyphenols [2,3]. Within polyphenols sources, the *Curcuma* genus have acquired great importance mainly due to the presence of curcumin, a compound with anti-inflammatory and antioxidant properties, recognised as valuable for the treatment/prophylaxis of ARND [2,3]. In a first step of our research, using a multi-technique biophysical study, curcumin revealed a weak pharmacokinetic profile with low bioavailability and solubility, bioac-cumulation, high affinity to human serum albumin, as well as a tendency to induce membrane biophysical changes [4]. Therefore, to improve the bioavailability of curcumin and consequently its therapeutic benefit, this study aimed to encapsulate curcumin in stealth nanocarriers (NC) of dioctadecyldi-methylammonium bromide (DODAB) and 1-oleoyl-*rac*-glycerol (MO) (1:2) (Figure 1).

The NC present high encapsulation efficiency. Also, by dynamic/electrophoretic light scattering and nanoparticle tracking analysis, the NC developed exhibited sizes lower than 200 nm, high stability when stored up to 4 months and a positive superficial charge, allowing the permeation of the blood-brain barrier by absorption-mediated transcytosis, which increases their interest for ARND biomedical purposes.

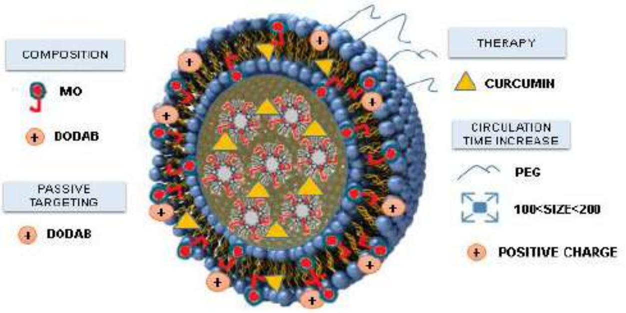

Figure 1: Schematic representation of the developed formulation.

An *in vitro* biphasic controlled release, of 94,5% of curcumin (R^2=0,998) after 50 h was also observed. Furthermore, after successful PEGylation, the ability to prevent interactions with plasma proteins, was also confirmed. Moreover, by fluorescence decay of a lipophilic probe (DPH-PA) under the action of a peroxyl radical generator (AAPH) the antioxidant activity was confirmed.

To study *in vitro* the efficiency of NC we are performing studies in neuronal cells, and analysing the concentration-toxicity curves of curcumin, empty NC and curcumin loaded NC in human SH-SY5Y cells using two cytotoxicity assays: dimethylthiazol diphenyltetrazolium (MTT) reduction and neutral red (NR) uptake.

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MgAPO-based nanostructured materials: in the search of one-directional antenna systems.

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Mimicry of natural processes, such as photosynthesis, has always attracted scientists. However, the synthesis and design of artificial antenna systems is not an easy task. In natural antenna systems, light-energy is harvested and transferred sequentially from a donor to an acceptor, usually chromophores [1]. In this work, artificial antenna systems consisting on different chromophore species *in situ* encapsulated into 1-D nanochannelled magnesium-aluminophosphates (MgAPOs) are synthesized and characterized. In these hybrid materials Fösters Resonance Energy Transfer processes take place between dyes or dye species absorbing and emitting light in different ranges of the electromagnetic spectrum. Furthermore, through the crystallization inclusion method approach, the encapsulation of the dyes is not only performed in a unique step, but also a strategic distribution of the dye species along the nanochannells of the host is achieved, with J-aggregates in one edge of the particles and monomers in the opposite end (Figure 1), enabling a one-directional energy transfer from monomers to aggregates. Following this strategy, different hybrid materials were achieved, incorporating pyronin Y (PY) and/or acridine (AC) [2,3]. The energy transfer in these materials has now been experimentally evidenced by remote excitation microscopy technique [4]. However, in the search of an antenna system in which the energy transfer reaches a longer distance, a material containing a cyanine dye (PIC) with J-aggregates showing intriguing properties, was prepared. A more efficient antenna system was achieved as a result, in which the energy transfer reaches over tens of microns (Figure 2) [4].

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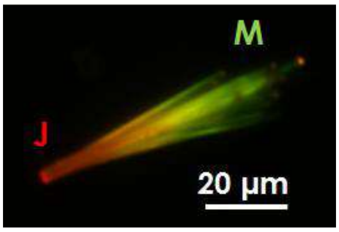

Figure 1: Fluorescence image of a PY/MgAPO-36 particle bouquet under blue excitation.

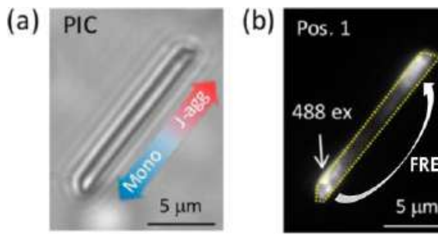

Figure 2: Transmission (a) and fluorescence intensity image (b) of a PIC/MgAPO-36 particle. 488 nm excitation was fixed at position pointed with an arrow.

Tuball ™ Single wall Carbon Nanotubes: Health, Safety & Environmental status

Presenting Author Van Kerckhove Gunther
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The company OCSiAl is been founded in 2009 and is also the first SWCNT manufacturer who has completed his EU-REACH registration for a tonnage band of up to 10T/a. Later on this year we will be placed on the US-TSCA inventory, our PMN file will be dropped meaning we will have a signed consent order with the EPA.
Because Tuball™ is used and also tested in various applications on an ongoing basis, also receiving a lot of interests worldwide. That is why it is obvious that the company OCSiAl is establishing the necessary regulatory and quality standards worldwide.
The first part of this presentation will aim at providing a short introduction of our Tuball™ substance and his product line, a second part of the presentation will be an overview of the status and plans of the ongoing registrations an compliance. The third and last part of the presentation will focus on the health, safety and environmental aspects of our Tuball™ substance and the different applications.
As SWCNT manufacturer, OCSiAl is doing continues investments in improving our understanding of our different (new) Tuball products themselves and potential hazards through their (entire) life cycle. We are involved in generating additional test data and collaborating with industry associations and networks.

This presentation will describe the steps being taken by the company H&S Lead manager, Van Kerckhove Gunther to successfully introduce our carbon nanotubes (SWCNT's) regulatory status and outline our (future) plans for numerous of studies and qualifying our Tuball™ substance including the different kind of compositions.

References

[1] Mandatory testing for different notifications worldwide
[2] Characterization & physical analysis managed by our own R&D centre.

Figures

O C Si Al
carbon nanomaterials for the global industry

Figure 1: Company OCSiAl

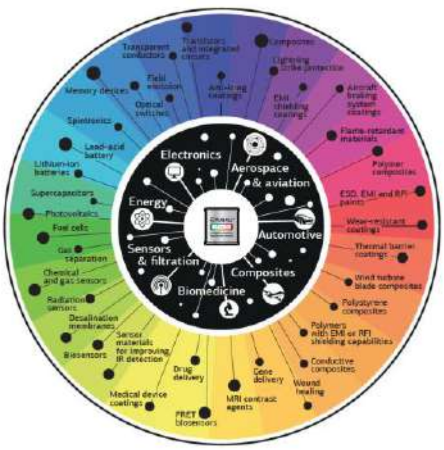

Figure 2: SWCNT substance type – one additive for thousands of materials

Ensuring safety when scaling-up nano-based processes: the case of printed electronics

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Abstract
Scaling up nano-based processes is fundamental to ensure the growth of the nanotechnology-based industry and to attend market demands. The concept of Safe-by-Design underlines that safety should be considered in an integrated way right from the earliest phases of the research and innovation process. Following this concept, in this paper we present the work currently on going to achieve safe pilot plants for printed electronics. This work is being done inside the Horizon 2020 INSPIRED project (grant agreement nº 646155).

The strategy followed is described in Schimpel et. al (2017) [1]. It basically consists of a risk assessment approach that includes six steps (Figure 1): (i) Information Gathering; (ii) Hazard Assessment, to collect info on the nanomaterials toxicology; (iii) Exposure Assessment, to identify exposure scenarios for both, workers and the environment; (iv) Risk Characterisation, using state-of-the-art approaches and control banding tools such as ECETOC TRA, Stoffenmanager Nano and ISO/TS 12901-2:2014; (v) Refined Risk Characterisation and Exposure Monitoring, following the tiered approach proposed by the OECD (2015) [2]; and (vi) Risk Mitigation Strategies. This approach is implemented in all the processes involved in the life cycle of electronic inks from the synthesis of the nanomaterials to the final device end of life.

Results achieved up to now show that in general the processes have low risk ratios since nanomaterials are mainly handled in water dispersions and adequate engineering controls are kept. Workers' exposure in selected activities has recently been measured to check the appropriate performance of the implemented controls. More specifically, we monitored the graphene and silver nanowire synthesis and ink formulation handling. Data analysis is currently on going, but no relevant emissions of airborne particles in the workplace are expected. Results of this work will be presented.

Within the INSPIRED project, safety is considered during the scale up of printed electronics production; following this prospective approach, the potential impacts caused by the use of nanomaterials to workers and the environment can be effectively minimized.

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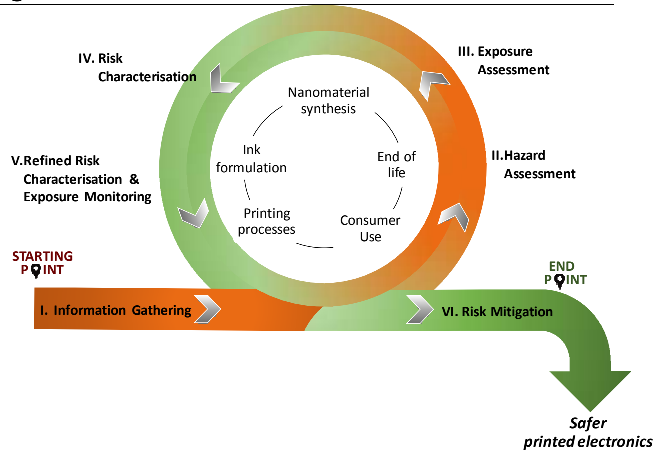

Figure 1: Strategy for risk assessment

Controlling Colour and Effective Refractive Index of Metal-Anodic Aluminium Oxide-Al Nanostructures: Morphology of AAO

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In the last years, the development of brilliant colours has produced immense interest to generate the colours found in nature. There are two approaches to perform artificially brilliant colours, chemical and physical. In the chemical coloration, pigments and/or dyes are used. The physical approach consists to metal-dielectric-metal nanostructures being environmentally friendly. In this case, the colour is due to the interaction of light with periodic nanostructures (anodic aluminium oxide). Metal-AOO-Al nanostructures can be used in different applications such as Surface Plasmon resonant, optical interference, wavelength absorbers, RGB display devices, optical sensors. In this study, metal-anodic aluminium oxide (AAO)-Al nanostructures were obtained by two steps, chromium thin films were deposited using sputtering system and self-ordered AAO films were fabricated using a two-step anodization process in different electrolytes in order to control the pore diameter, interpore distance and porosity[1]. The UV-Vis reflectance as function of the thickness for the different electrolytes of metal(Cr)-AAO-Al films was analysed in order to obtain the colour diagram of the films. The effective refractive index of AAO-Al films as function thickness, electrolyte, pore diameter, interpore distance and porosity (see Figure 1) was calculated from the UV-Vis reflectance. The aim of this work is to study the dependence of morphological parameters on the effective refractive index of AAO films [2].

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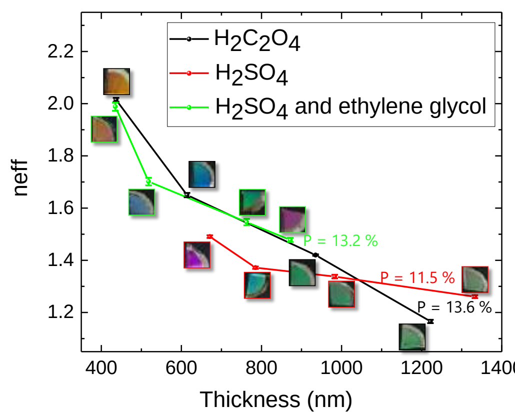

Figure 1: Effective refractive index as a function of the thickness for the different anodization conditions, and then different electrolytes. Colours of the metal-anodic aluminium oxide (AAO)-Al nanostructures.

Quantum transport simulations of graphene non-local spin valves

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Graphene is a promising platform for transporting spin information due to its high carrier mobility and low intrinsic spin-orbit coupling. State-of-the art devices have already demonstrated room temperature long spin lifetimes of several nanoseconds and spin diffusion lengths up to a few tens of μm [1]. The spin relaxation mechanisms have been founded to be strongly monitored by spin-pseudospin entanglement and dephasing effects [2]. The next challenge is to be able to manipulate and control spin signals to engineer active spintronics and hence envision complex graphene-based, non-charged-based devices [3]. Placing graphene on top of ferromagnetic insulators or transition metal dichalcogenides (TMDC) is a promising route to induce, by proximity effect, magnetism or strong spin-orbit coupling (SOC) in graphene while conserving the excellent electronic properties.

In this work, common experimental devices to measure spin-related properties, such as Hanle non-local spin valves (Figure 1)[4], are simulated in graphene within the Landauer-Büttiker formalism using the Kwant python package [5]. Such software is capable of simulating Hanle setups using fully coherent quantum transport. Comparison and discussion with available experimental data are presented for different graphene systems as well as computing local properties like (spin) currents and local density of states. In this way, a more microscopic picture of the spin-dynamics in graphene is obtained [6].

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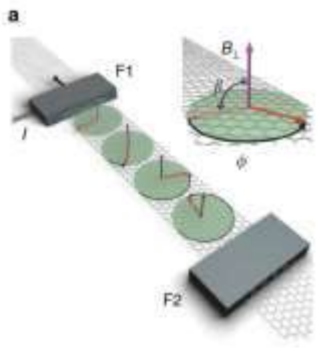

Figure 1: Schematics of the spin precession in a non-local Hanle measurement. Figure extracted from ref. 4.

Optically active hybrid nanostructures based on semiconductor quantum dots and chiral molecules for biomedicine

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Abstract

Unique optical properties of colloidal semiconductor quantum dots (QDs) allow to use them as a basis for hybrid nanostructures (HyNSs) with organic molecules for a wide range of biomedical applications: from highly sensitive biosensor devices to a new generation drugs [1].
A molecule, which is a part of HyNSs, may be chiral (has two mirror-image forms, known as enantiomers, which are not superimposable in three dimensions). Chirality plays a crucial role in biology, chemistry, pharmacology, and medicine since most of the biomolecules and drugs are chiral [2]. In HyNSs, optical activity of a molecule and QD can be affected by each other [3]; that could also potentially lead to functional properties changes.
Here we report the studies on interactions between semiconductor QDs and chiral molecules (cysteine, chlorin e6) (Figure 1, Figure 2). It was found that the optical activity of both QDs and molecules inversely depends on the distance between them in HyNSs. Our future work will involve investigation of the correlation between chiroptical and functional properties of HyNSs.

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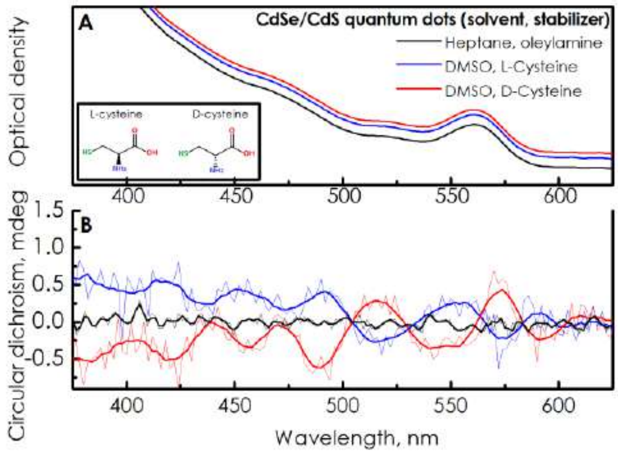

Figure 1: Comparison of (A) absorption and (B) circular dichroism spectra of QDs stabilized with achiral and chiral ligands.

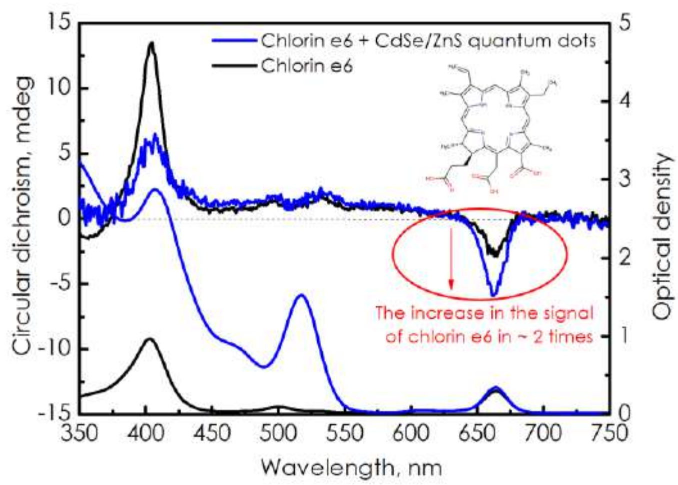

Figure 2: Absorption and circular dichroism spectra of HyNSs based on QDs and chlorin e6 in comparison to that of with free chlorin e6.

NANOSPAIN2018 – POSTERS

Micro-nanotextured omniphobic surfaces on aluminum and polyMER

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Abstract

Omniphobic surfaces are highly demanded for a wide range of applications in different industrial sectors, where polymer materials are gaining representability. Metallic material like aluminium is widely used in industry by itself and, at the same time, as prototype moulding tool for plastic injection moulding. In these materials hydrophobic/oleophobic functionalities can be addressed through surface micro-nanostructure modification combined with chemical composition (through coating or additives). Surface micro-nanostructure must be defined through micro and nano features combination if optimum hydrophobic/oleophobic behaviour is targeted.

Aluminium surface modified through dislocation etching shows a very interesting omniphobic behaviour. Its replication on polymer surfaces seems to keep similar properties. At the same time, durability of such functionality is being addressed and will be presented as it is a critical issue for its applicability in industrial sectors.

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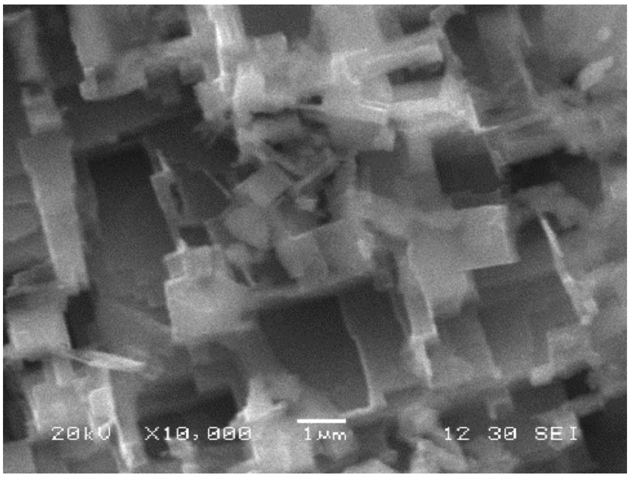

Figure 1: SEM image of the surface of etched aluminium

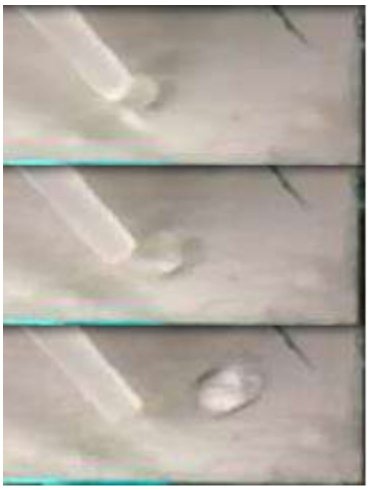

Figure 2: Consecutive images of droplet rolling on micro-nanotextured PC surface

Microencapsulated natural antioxidants as depollutant materials

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Abstract

Hexavalent chromium is a substance harmful to health, which Directive 98/98/EC classified as a Category 1 carcinogen by inhalation, while direct contact with the skin produces the same effect. In addition, hexavalent chromium is also classified as an allergenic compound. The maximum concentration of chromium (VI) allowed for direct contact with human skin is laid down by Regulation (EU) 301/2014 (amending Annex XVII to Regulation EC N° 1907/2006 of the REACH).
Hexavalent chromium is used for the production of stainless steel, textile dyes, wood conservation, leather, and as anti-corrosion coatings, among other applications.
The current chromium pollution problem is due to an uncontrolled discharge of chromium to the environment. This uncontrolled discharge is caused mainly by collecting systems from industrial wastewater effluents. Although specific technological processes for the removal of heavy metals from wastewater have been developed, their implementation is highly expensive and these compounds are very often employed in the industry.
This study proposes a solution to reduce the presence of chromium (VI) in wastewater by a reduction process from chromium (VI) to chromium (III), based on the use of natural antioxidants.
Nevertheless, the problem of using antioxidants is their low resistance to the technological processes and the different environmental conditions, such as the pH, the oxygen in the atmosphere or the temperature. In this sense, microencapsulation technology could increase the shelf life of a bioactive substance, such as antioxidants, and promote their controlled release under pre-established conditions.
In this study, a modified complex coacervation technique has been used for the microencapsulation of different natural antioxidants. The results obtained indicate that synthesised microcapsules are able to reduce up to 99% of the hexavalent chromium present in aqueous media in short contact times and low concentrations.

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Graphene as lubricant additive of ionic liquids

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The rheological characterization of ionic liquids has awaken a strong interest in the scientific community since this is one of the principal features to be taken into account for tribological applications [1]. In a Newtonian flow, shear stress is proportional to shear rate and the viscous behavior is not affected by shear rate. In the case of fluids with certain degree of phase ordering, the non-Newtonian phenomenon is typically prevalent. Shear thinning of ILs has been reported previously in the literature because of the existence of liquid phase aggregates or networks [1,2]. The usage of carbon nanosystems as modifiers of the behavior of ionic liquids has increased these last years, leading to a number of relevant studies. The development of large numbers of new ILs with many different technological applications and their ability to disperse the different carbon structures are among their main advantages [3]. In this work, we present the rheological characterization of dispersions of carbon nanotubes in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. We have evaluated the effect of addition of graphene and temperature on the viscosity under shear rate. The dispersion has an anomalous increasing of the viscosity when the temperature is raised at high graphene concentrations (Figure 1). Furthermore, these nanofluids have been tested as lubricants with and outstanding tribological behavior (Figure 2).

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Figures

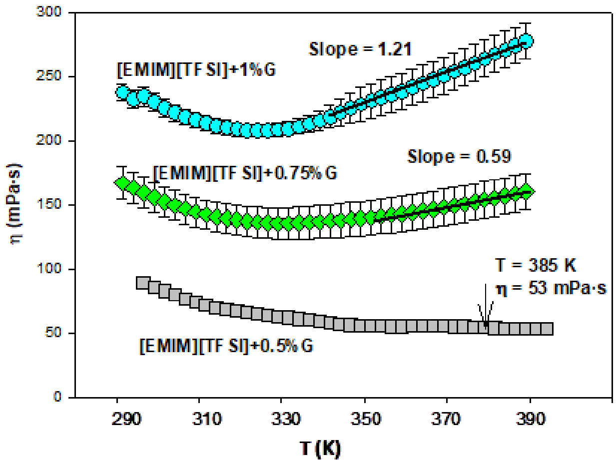

Figure 1: Temperature dependence of viscosity with the addition of graphene.

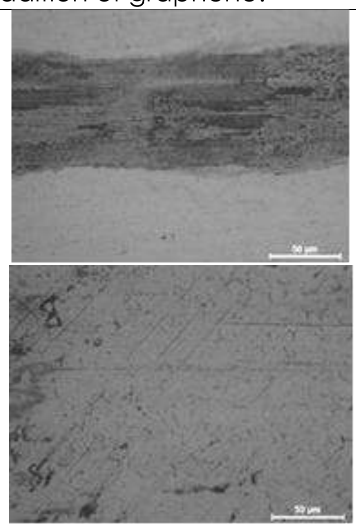

Figure 2: Wear track of the ionic liquid and the 1 wt.% graphene dispersion on ceramic-steel contacts.

Thermal behaviour of screen-printed graphene based pastes

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Resistive heating is the process by which an electric current pass through a conductive material (the resistor) and releases heat. Carbon based inks and pastes are promising materials [1][2] for this application due to their self-limiting behaviour with the temperature and because they can be printed on a variety of surfaces [3]. This work analyses the thermal behaviour of different carbon formulations on glass.

Four different materials are being tested. All of them are based on graphene (GNP and rGO) as well as CNT derivatives. Glass has been selected as the substrate to analyze the thermal behaviour of those pastes. Voltages up to 220 V are applied to the deposited material and the temperature increase is registered with a thermographic camera.

Current work is being performed comparing the behaviour of the four formulations in a simple pattern, a linear resistance. Preliminary results obtained with one of the formulations deposited in glass are shown in Fig1. An increase of more than 10 degrees is registered in few minutes when 30 V were applied, whereas when applying 220V the increase is too fast and the glass breaks. Different parameters, as thickness, resistivity and the composition are analysed. The goal is to identify optimal formulations for resistive heating applications.

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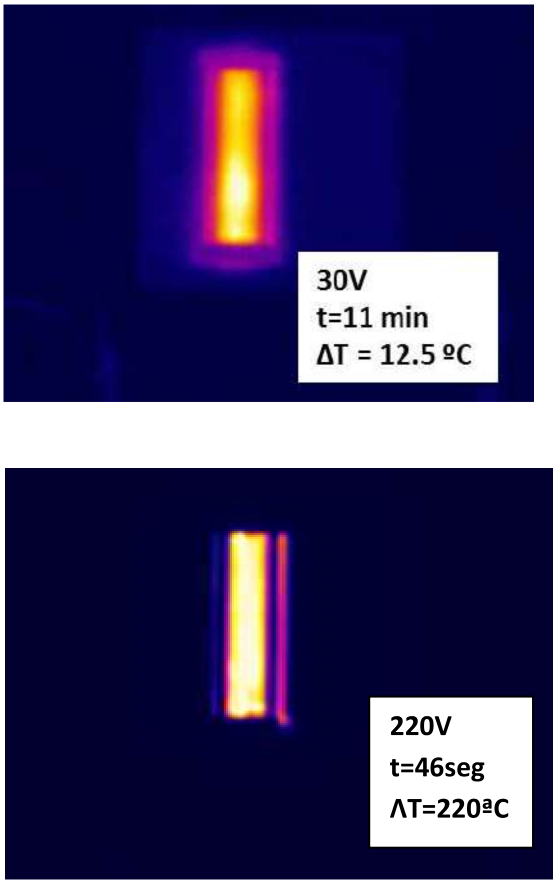

Figure 1: Thermographic image obtained with a graphite paste

Engineering of magnetic properties of Co-rich microwires by Joule heating

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The performance of magnetic devices can be significantly improved if the used materials will present higher GMI effect. Considering that the predicted theoretical maximum GMI ratio (about 3000%) [1] is few times superior to the experimentally reported it is expected that technology improvement involving development of effective post-processing method will allow achievement of higher GMI ratio. Consequently considerable efforts have been paid to studies of the post-processing on GMI ratio of various magnetic materials, such as wires, ribbons, thin films and multilayers [2].
It is expected that Joule heating due to the induced magnetic anisotropy [3] can further improve the GMI effect. Up to know only limited number of experimental results on effect of current annealing on GMI effect are reported [2]. Additionally, the best GMI performance is observed in amorphous magnetic wires exhibiting excellent magnetic softness. Current annealed $Co_{67}Fe_{3.9}Ni_{1.5}B_{11.5}Si_{14.5}Mo_{1.6}$ microwires present excellent magnetic softness with low magnetic anisotropy field of about 25 A/m and coercivity of 2 A/m (see Fig. 1).
We have investigated the GMI response of the current-annealed glass-coated microwire. From the obtained dependence we determined the optimal current annealing conditions and obtained considerable improvement of $\Delta Z/Z_{max}$ – values from 550% to about 650% after appropriate current annealing conditions (see Fig. 2).

The analysis of the GMI ratio as a function of the frequency opens new lights to understand the distribution of the magnetic anisotropy inside the microwire.

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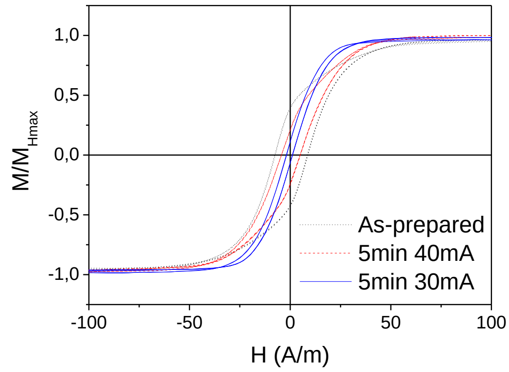

Figure 1: Hysteresis loop of as-prepared and current annealed $Co_{67}Fe_{3.9}Ni_{1.5}B_{11.5}Si_{14.5}Mo_{1.6}$ amorphous glass-coated microwire.

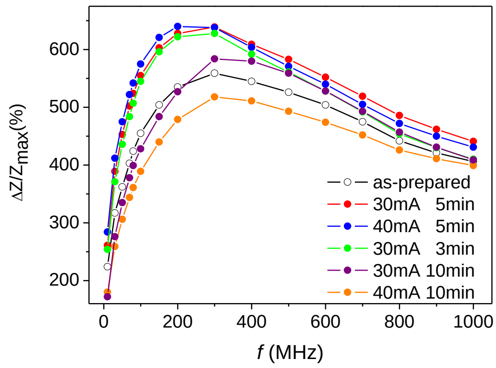

Figure 2: $\Delta Z/Z_{max}(f)$ dependences observed in as-prepared and current-annealed microwire at different annealing conditions.

Sudoe NanoDesk Observatory on Nanotechnology Applications and Safety in the Plastic Sector

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The Sudoe NanoDesk Observatory on Nanotechnology Application and Safety in the Plastic Sector is a web tool aimed at the analysis, dissemination, use and exploitation of information of strategical value for the decision-making of companies and institutions.
The goal of the portal is to promote technical viability and safe use of nanotechnology in the plastic sector, taking advantage of the results of the NanoDesk project and contributing directly to their dissemination.
The development of the observatory was carried out considering the information needs of the target groups, including microenterprises, SMEs, industrial associations, and research organizations, competent authorities, promoting decision-making based on recent knowledge.
The portal is structured in different thematic priorities to be aware of new tendencies reading the latest news and learn how to safely handle nanopolymers, covering:

→ Technological surveillance of the applications and processing of NMs in the plastic sector.
→ Safety of processes and products: toxicological aspects, occupational exposure and risks for the consumer.
→ Latest news of the sector, such as publications, scientific articles or patents.
→ Financing and subsidies opportunities.

The portal contributes directly to the promotion of technical feasibility and the safe use of nanotechnology in the plastic sector, the specific objective of the project. The compilation of information is possible using an intelligent search engine for applications and risks of nanotechnology based on data mining techniques to gather information from existing online publications.

Figures

Figure 1: Overview of the observatory with the different sections

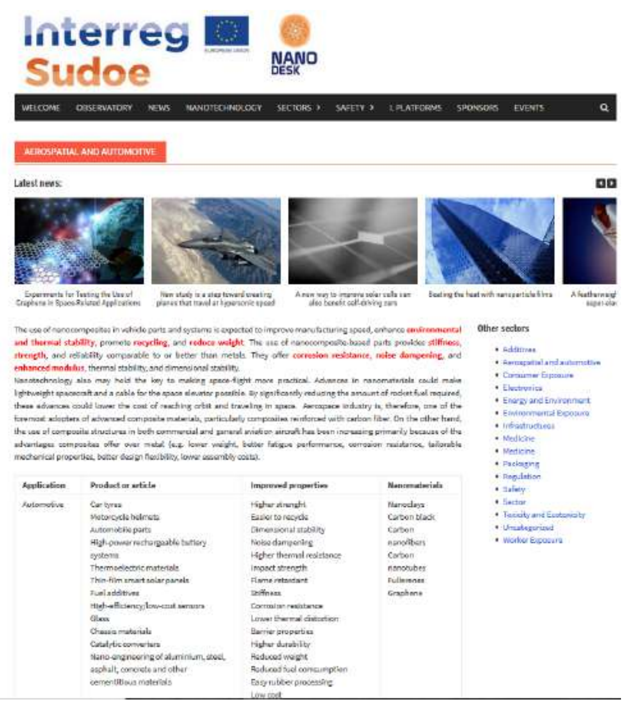

Figure 2: Each industrial sector filters the news, applications and events related to it.

Risks derived from the use of nanomaterials in 3D printing of scaffolds

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3D polymer printing has opened new possibilities for developing scaffolds for bone tissue regeneration. Nanocomposites filled with layered hydrotalcite, zirconium phosphate, nanohydroxyapatite and reduced graphene oxide have been produced to enhance the scaffolds functionalities. Workers involved in the different manufacturing processes can be exposed to nanoparticles. In this work, the potential risks for workers derived from the use of nanomaterials during new scaffolds manufacturing are analysed. This work has been carried out in the frame of the Horizon 2020 FAST project (grant agreement no 685825)

The two components of risk, hazard and exposure are being analysed.
Cytotoxicity assessment of the four above mentioned nanofillers has been carried out on five different cell lines, representing main exposure routes (MRC-5 fibroblast, liver HepG2, skin-3T3, and monocytic cell line THP). According to the results, the toxicity of the fillers is cell dependent. The lowest Ic50 values have been observed for rGO samples and highest ones for Zirconium phosphate nanoparticles.

Occupational exposure to nanomaterials is being evaluated following the tiered approach proposed by the OECD (2015) [1]. Work performed includes the identification of exposure scenarios in the processes involved, from nanoparticles synthesis to 3D printing. Qualitive risk assessment has been performed to identify key exposure scenarios using control banding tools such as Stoffenmanager Nano and CB nanotool [2]. Results showed that, in general, scenarios have low risk profiles since nanomaterials are handled as dispersions or fixed in polymer matrices. Furthermore, adequate, engineering controls are implemented. Future activities will include the quantitative assessment of workers exposure during graphene production.

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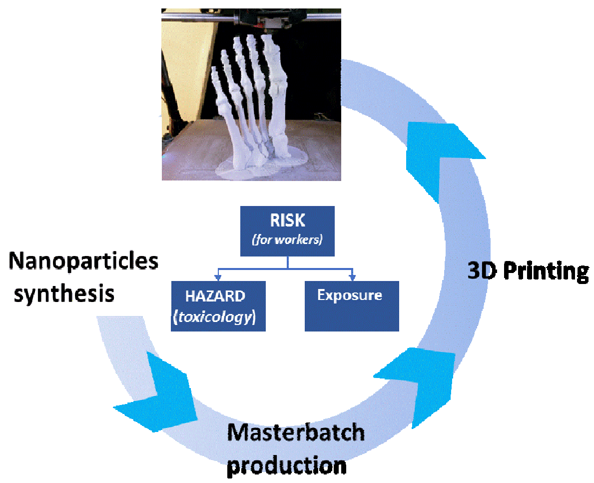

Figure 1: Risk assessment in FAST project

Curcumin-in-epiβcyclodextrin double-loaded liposomes: selection of size reduction methodology

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Curcumin (cur) is a natural antioxidant, anti-inflammatory and anti-tumoral compound with extremely low solubility in water and bioavailability [1]. Two simple ways of improving these properties are liposomes and cyclodextrins, such as epichlorhydrin-β-cyclodextrin. In previous works, we have demonstrated that the optimal composition for double-cur-loaded liposomes is the combination of 1 mg of curcumin and 4 mg of estearylamine in the bilayer, and cur-epi-β-cyclodextrin in the aqueous compartment. However, the size reduction method was not clearly elucidated. Based on these premises, double-cur-loaded liposomes have been extruded or sonicated at three different levels. Firstly, multilamellar vesicles were prepared by thin-layer evaporation method described by López-Pinto et al. [2]. Extrusion was performed at 58°C using polycarbonate filters with three different pore sizes (800, 400 and 200 nm). Samples were extruded 5, 9 or 13 times from each filter. Sonication was performed at 58°C for 10, 20 and 30 minutes with an in-between pause of 1 min at room temperature every 10 min. A sample without size reduction treatment was made as control formulation. Techniques of photon correlation spectroscopy and DLS were applied for size and z-potential. Encapsulation efficiency (EE) and recovered PC were calculated, as previously reported González-Rodríguez et al. [3]. Results showed that liposomes sonicated more than 10 min (runs 2 and 3) have a tendency to leakage over time, while in those extruded (Run 4-11) EE decreases by 30% or more in all cases, except for those extruded 5 times using an 800 nm pore-sized filter (Run 4), which obtained similar EE than liposomes sonicated for 10 minutes (Fig 1.). Although the mechanical procedure of both techniques affect the integrity of the bilayer, also the thinning and loss of elasticity that curcumin provokes when it is imbibed in bilayers [4-6], could trigger this leakage. Thus, liposomes extruded 5 times using an 800 nm pore-sized filter was selected as optimal formulation for further studies.

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Figures

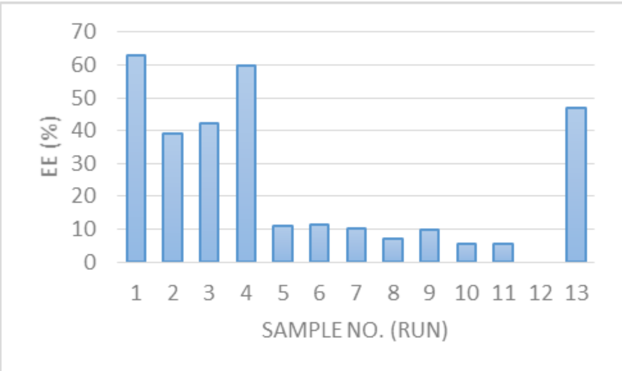

Figure 1: Encapsulation efficiency of each sample. Run 1 to 3 where sonicated. Run 4 to 11 where extruded. Run 13 is the control sample. Run 12 cannot be performed.

European Project JOSPEL develops low energy passenger comfort systems based on the Joule and Peltier effects

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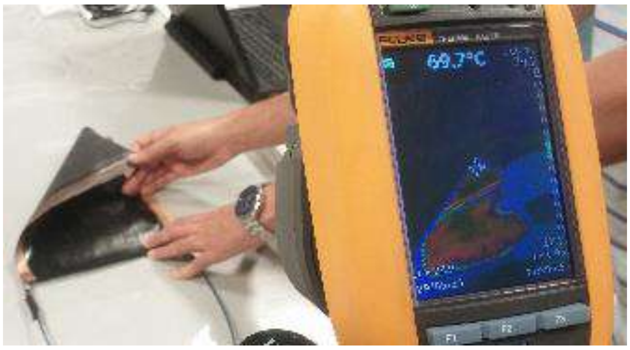
Abstract

Electric vehicles require specific thermal management solutions because their motors and batteries do not create heat in the same way as internal combustion engines. Up to 25% of the potential electric vehicle's range is reduced due to the use of current HVAC (heating, ventilation, and air conditioning) technologies. The main objective is the reduction of at least 50% of energy used for passenger comfort (<1,250 W) and at least 30% for component cooling in extreme conditions with reference to electric vehicles currently on the market.
Joule heating is the process by which the passage of an electric current through a conductor releases heat. The amount of heat release is proportional to the square of the current. Heating fabrics and panels are being develop aiming to achieve an efficient heating in the cabin. Heating is achieved with low energy consumptions. Latest results will be presented in the workshop.

Figures



- Voltaje range: **5 volts** to **220 volts** AC or DC
- Power range: Up to **2000 Watts/m^2**
- Temperature range: Up to **100ºC**
- Temperature increase: ~50ºC (in less than one minute)

Figure 1: Heating fabric performance

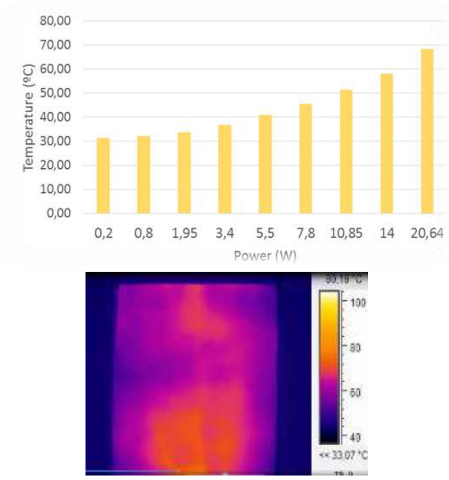


Figure 2: Heating panel performance

Long-chain unsaturated sphingolipids: a glimpse into lipid complexity through AFM, DSC and fluorescence

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The effects of C24:1 sphingolipids have been tested in phospholipid bilayers containing cholesterol. Confocal microscopy, differential scanning calorimetry (DSC), and atomic force microscopy (AFM) techniques have been used. More precisely, the effects of C24:1 ceramide (nCer) were evaluated and compared to those of C16:0 ceramide (pCer) in bilayers composed basically of dioleoyl phosphatidylcholine, sphingomyelin (either C24:1, nSM or C16:0, pSM) and cholesterol. Combination of equimolecular amounts of C24:1 and C16:0 sphingolipids were also studied. Results show that both pCer and nCer are capable of forming segregated gel domains. Force spectroscopy data point to nCer having a lower stiffening effect than pCer, while the presence of nSM reduces the stiffness. DSC reveals Tm reduction by nSM in every case. Furthermore, pSM seems to better accommodate both ceramides in a single phase of intermediate properties, while nSM partial accommodation of ceramides generates different gel phases with higher stiffnesses caused by inter-ceramide cooperation (Figure 1). If both pSM and nSM are present, a clear preference of both ceramides towards pSM is observed. These findings show the sharp increase in complexity when membranes exhibit different sphingolipids of varying N-acyl chains, which should be a common issue in an actual cell membrane environment [1,2].

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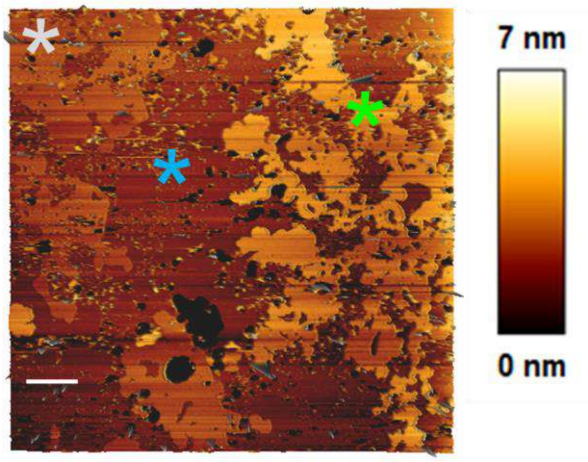

Figure 1: DOPC:nSM:Chol (2:1:1) + 15% nCer + 15% pCer bilayer (AFM height image). Each ceramide appears to segregate into different domains that can be distinguished by height (asterisks in the image) or by nanomechanical resistance but not by RhoPE fluorescence (see Poster).

New magnetic nanocomposites for theranostic applications

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Abstract

Nanostructured materials are of increasing interest in biological and biomedical applications in recent years[1]. Currently, promising strategies are being developed that aim at combining diagnosis and therapy capabilities into clinically effective formulations[2]. There is a growing interest in developing smart theranostic platforms that can concurrently diagnose disease, externally trigger treatment and monitor response. A range of different hybrid systems have been proposed within the scientific community as bioactive encapsulating agents and carriers due to their biocompatibility, low toxicity and ability to influence the delivery profile of pharmacological agents[3,4]. In this context, hybrid organic-inorganic magnetic nanocomposites (mNCs) are being explored to synergistically combine the modified bioactive release provided by the organic encapsulation and the intrinsic physico-chemical properties from the inorganic counterpar[5].

Here, we present new drug loaded magnetic nanocomposites showing good multifunctional performance as heat generating sources in magnetic hyperthermia (MH) therapy, T2-contrast agents in magnetic resonance imaging (MRI) and responsive drug delivery vehicles. Their design, synthesis and physicochemical characterization will be shown, as well as their biocompatibility and functional validation in vitro. The high ability to simultaneously encapsulate both therapeutic agents and magnetic nanoparticles enables an external control over the drug release profile and opens the door to personalized oncology through integrating tumor diagnosis and therapy. The outstanding performance shown by mNCs *in vitro* allows to propose them as next generation drugs for the diagnosis and therapy of cancer.

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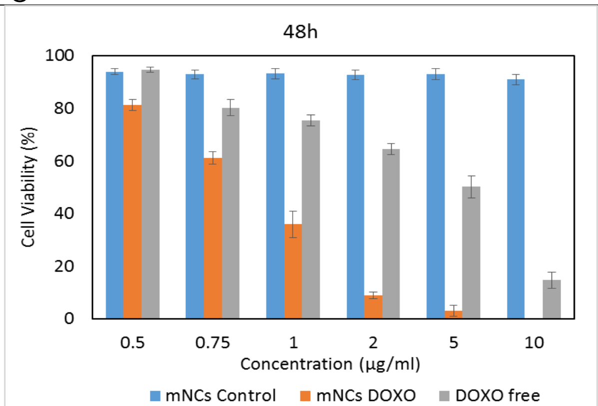

Figure 1: Viability of breast cancer cells. mNCs encapsulated with doxorubicin induced enhanced apoptosis of the cells, showing better results than free drug.

Copper oxide thin films with high transparency and p-type conductivity

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Abstract

Cu_2O and CuO are p-type semiconductors attracting renewed interest in multiple applications: catalysis, batteries, solar cells, etc. [1-3], because of their inexpensive and non-toxic composition, together with their adjustable gap energy (in the 1.4-2.6 eV range) and hole density controlled by copper vacancies [4]. The optical and electrical characteristics of copper oxide thin films are greatly dependent on the preparation procedure, which determines the crystallite size and the native defects.

In the present work, Cu_2O and CuO thin films have been obtained by heating evaporated copper in air at a suitable temperature. Cubic Cu_2O with mean crystallite size ~14 nm is obtained at 250 °C (figure 1), below the temperature expected from the equilibrium diagram [5]. The increment of the heating temperature up to 350 °C produces transition to CuO with monoclinic symmetry and ~16 nm crystallite size.

Both Cu_2O and CuO thin films show transparency above 85 % in the near infrared region (figure 2). In the visible range, the optical absorption is higher for CuO (with E_g= 1.4 eV) than for Cu_2O (E_g= 2.6 eV). The p-type conductivity is above 10^{-2} S/cm for Cu_2O and below 10^{-3} S/cm for the CuO.

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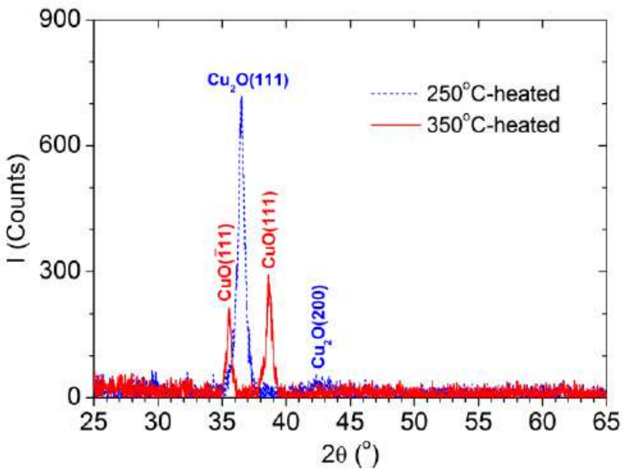

Figure 1: X-ray diffraction patterns obtained for the evaporated Cu thin films after heating in air at different temperatures.

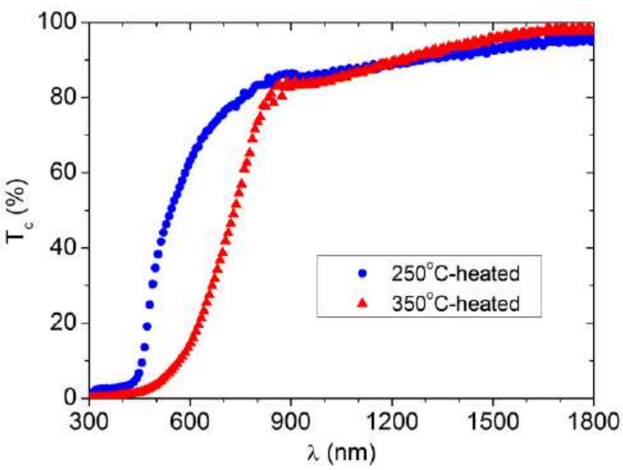

Figure 2: Optical transmittance spectra (corrected by the reflectance losses) that have been obtained for the evaporated Cu films after heating in air at different temperatures.

NoCanTher: Nanomedicine Upscaling for Early Clinical Phases of Multimodal Cancer Therapy

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BIOPRAXIS faces drug development for rare cancers, including glioma and pancreatic cancer, using nanotechnology and biological molecules like proteins and peptides. Moreover, is also working in controlled release systems through nanoparticles, which improve therapeutic action of APIS and allow protection of biological molecules and targeting. BIOPRAXIS and some European Entities have worked previously in this area in protects as THERAGLIO project (Contract n FP-602923), MULTIFUN a finished FP7 project and HEATDELIVER: Heat and and Drug Delivery nanosystem with active tumortargeting features (Eurotransbio project). Based on the knowledge obtained, project NoCanTher (H2020-685795) aims at translating one of these nanoformulations to early clinical development for pancreatic cancer. The therapy is based on the functionalization of iron oxide nanoparticles using a targeting peptide and anti-cancer drugs, together with the effect of hyperthermia generated by an external alternate magnetic field. To successfully reach this objective, we will concentrate our efforts in two main group of activities:

• Nanomedicine up-scaling under GMP conditions: NoCanTher will scale up the manufacturing of the proposed nanoformulation from milligram-scale laboratory synthesis up to multigram-scale production to generate sufficient material

for clinical and regulatory assays. To this aim, a GMP production line will be optimised and the relevant quality control will be conducted at the different stages of the up-scaling process.

• Clinical trial: NoCanTher will include late preclinical parameter testing to raise a clinical treatment protocol, regulatory assays, as well as the design of the clinical trial and the preparation of the Investigational Medicinal Product Dossier (IMPD). This strategy will allow us to apply for Clinical Trial Authorisation (CTA) then, we will carry out a Phase I clinical trial. NoCanTher involves the participation of institutions from three different sectors (academia, industry, clinical) and from five different countries (Ireland, France, Germany, Spain and the UK).

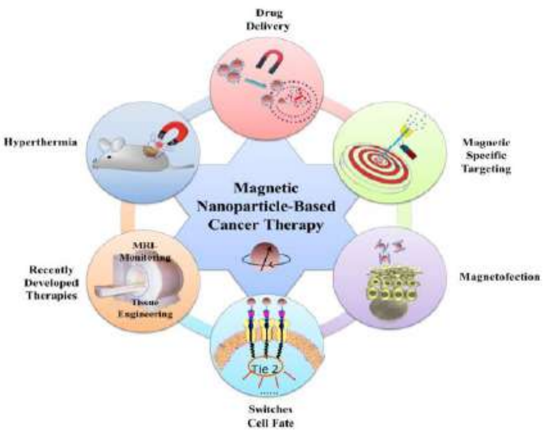

Figure1. Illustrating the process.

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Cross-sectioning nanofibers and detecting additives

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Abstract

The nanofibrous structures are widely researched nowadays in various fields - from electronics to medicine or pharmacy. Properties of synthetic or natural polymers used for electrospinning are often enhanced with additives or carry drugs or other active substances [1, 2]. But there are not many ways how to study distribution of the additives inside these fibers with diameter smaller than 1000 nm. The transmission electron microscopy could be used, but it does not determine whether the additives are on the surface or inside fibers. In this work we use the not so much used alternative - the ion beam slope cutting method to cut nanofibrous layers and make its cross-section available for further analysis. This slope cutting method is quite widely used in the field of metals analysis [3] and it is very promising also in the field of polymers, where it is used very rarely especially for nanofibers. Unfortunately, unlike the metals, the polymers behave very differently. Their specific behaviour requires a specific approach to perform the slope cutting. In this work we discussed the effects of various parameters of the ion slope cutting process on the nanofibrous layers. We also defined the best conditions of cutting process and the best way how to prepare a sample for ion cutting. Moreover, we used the energy dispersive X-ray spectroscopy to map cross-sections of our fibers and thus show distribution of additives.

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Figures

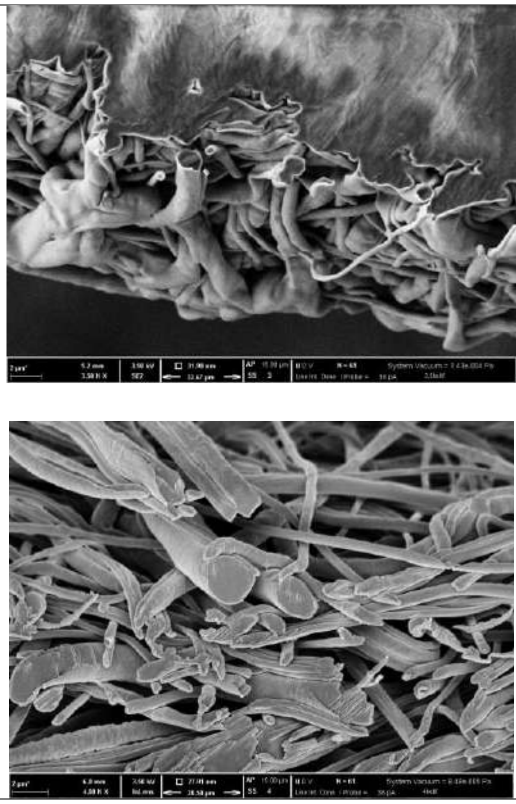

Figure 1: The cross-sections of the two polycaprolactone nanofibrous layers from a same sample cut under different conditions of the ion beam slope cutting method.

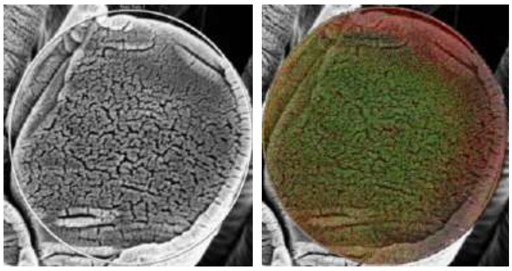

Figure 2: The cross-section of a single fiber with a the EDX mapping of carbon (red) as a polycaprolactone marker and bromine (green) as an additive marker.

Carbon nanotube-based targeting systems for cytoplasmic delivery

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The translocation of nanomaterials or complex delivery systems into the cytosol is a main challenge in nanobiotechnology.[1] Current nanodevices offer limited solutions to the problem of the cytoplasmic delivery of active compounds. The biggest challenges are i) specific cell recognition, ii) protection of the cargo from the hostile lysosomal chemical conditions, iii) nonlethal endolysosomal (E-L) escape, iv) the carriage of different particles or chemicals into the cytosol, and finally, v) clearance of the delivery vectors to avoid long-term cytotoxicity. To date, there is only partial understanding of how to control the intracellular fate of the carrier systems after endocytosis.
After receptor-mediated endocytosis, most delivery vectors are trapped in the endo-lysosomal vesicles,[2–4] where the hostile enzymatic and chemical conditions destroy the nanomaterials and/or inactivate the therapies,[5,6] or alternatively, undergoing exocytosis. We have explored a novel surface particle coating made of adsorbed carbon nanotubes (CNTs) that provides coated materials with new properties that reproduce the viral cell invasive mechanisms, namely: receptor mediated endocytosis, endo-lysosomal escape and cytosolic particle release preserving intact cell viability.
This fully biocompatible[7,8] novel biomimetic coating design will enable the **intracytoplasmic delivery** of many different nanomaterials thus, opening the door to a wide array of chemical and physical processes within the cytosolic or nuclear domains, and supporting the generation of new developments in the biotechnological, pharmaceutical and biomedical industries.

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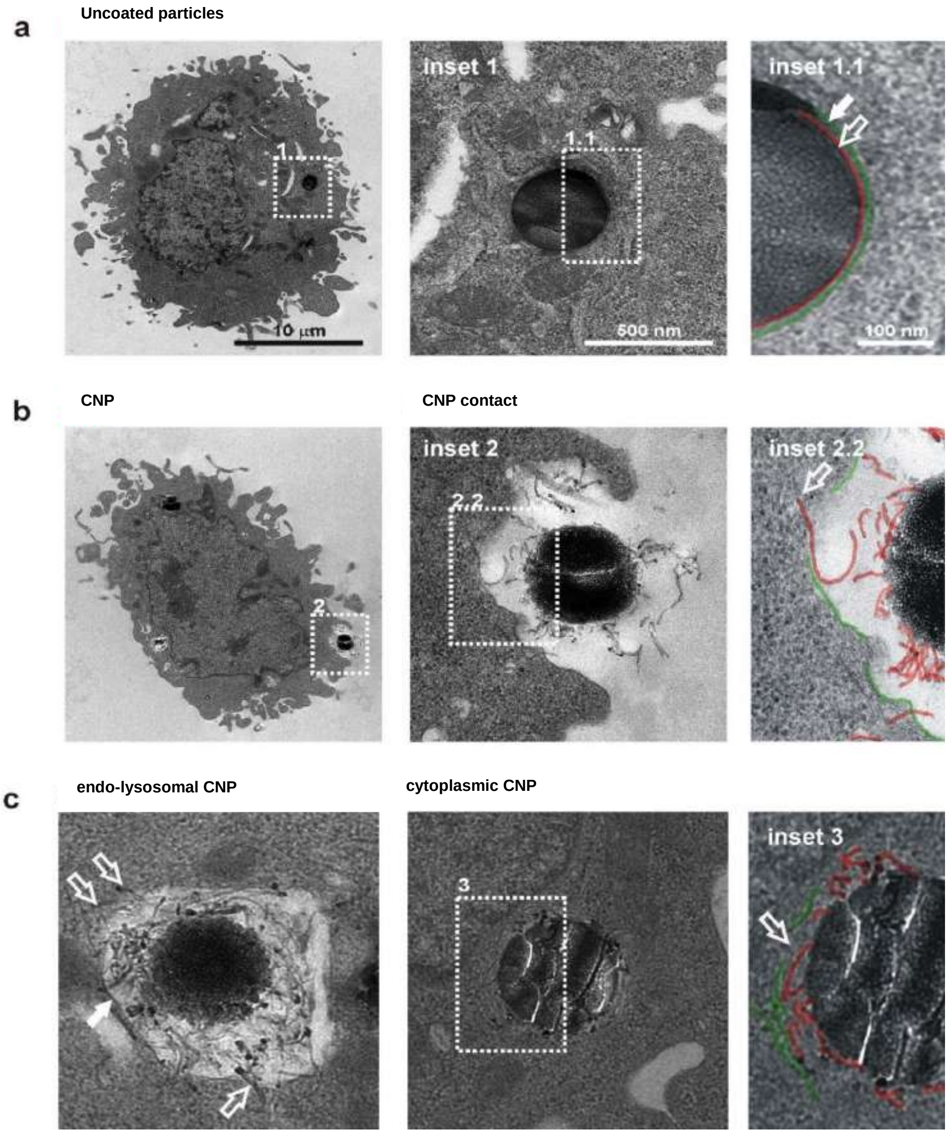

Figure 1: (a) TEM images of the cytoplasm of cells containing an uncoated particle. The endosomal membrane (pseudo-coloured in green) is clearly visible (solid arrow). (b) Section of a CNT-coated particle (CNP) contacting the surface of the HeLa cell. (Insets 2, 2.2) Some CNTs of the CNP coating (pseudo-coloured in red) are already penetrating into the cell cytoplasm (empty arrows). (c) Endo-lysosomal and cytoplasmic CNPs, Cytoplasmic CNTs and the membrane of the endosome are indicated with empty and solid arrows respectively. (Inset 3). More info in Refs. 7,8

Biophysical toolbox for nanotherapeutics characterization

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Nanotechnology has been fruitfully allied to medicine and pharmaceutical development; however many doubts persist regarding the efficacy and safety of nanotherapies (NTs). One of the concerns with NTs is that these innovative systems present increased surfaces and consequently are subject to greater interactions in our organism. In this context, one of the main challenges of Nanomedicine for the next 15 years is the development of methods that allow, using simple models, to predict the biological behaviour of NT [1]. *In vitro* assays may be interesting solutions in response to this challenge, since they allow the understanding of NT properties at the molecular level. Furthermore, under controlled conditions, the use of mimetic models of biological interfaces can help to rationalize and predict NT behaviours and their interactions *in vivo*.

This communication aims to present some routines developed within our research and entrepreneurship project [2,3] based in biophysical methods with spectroscopic detection units common to most research laboratories (fluorescence; UV-Vis spectroscopy). The routine assays presented constitute a helpful toolbox (Figure 1) for developers offering the possibility to study different interactions between therapeutic compounds and nanocarriers, as well as, accessing the interactions of the NTs developed with biointerfaces (membranes and proteins), as this is paramount in foreseeing NTs therapeutic and *off target* effects.

Figures

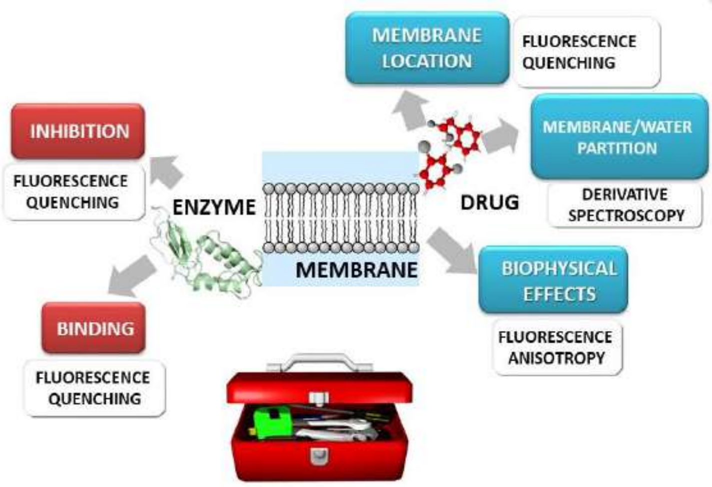

Figure 1: Biophysical toolbox for nanotherapeutics characterization

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GRAPHENE DISPERSIONS IN DILUTED IONIC AND NON-IONIC SURFACTANT AQUEOUS SOLUTIONS

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Abstract

Graphene (G) was dispersed in surfactant solutions of different nature: cationic hexadecyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB),non-ionic polyoxyethylene-23-lauryl ether (Brij L23), and anionic sodium dodecylsulphate (SDS). The influence of the surfactant type, chain length and concentration, G concentration and G/surfactant weight ratio on the fluorescence of vitamin B_2 (riboflavin) was investigated (Fig. 1). The quality of the dispersions was assessed by scanning and transmission electron microscopies (SEM and TEM) (Fig. 2). A quenching phenomenon of the fluorescence of riboflavin was found for G dispersions in all the surfactants, which generally becomes stronger with increasing G/surfactant weight ratio. For dispersions in the ionic surfactants, the quenching is more pronounced as the surfactant concentration raises, whilst for the non-ionic one remains merely unchanged for the different G/Brij L23 weight ratios. More importantly, results indicate that DTAB solutions are the optimum media for dispersing G sheets, leading up to 16-fold drop in the fluorescence intensity. Understanding the mechanism in fluorescence quenching of G dispersions in surfactants could be useful for several optical applications. [1]

Figures

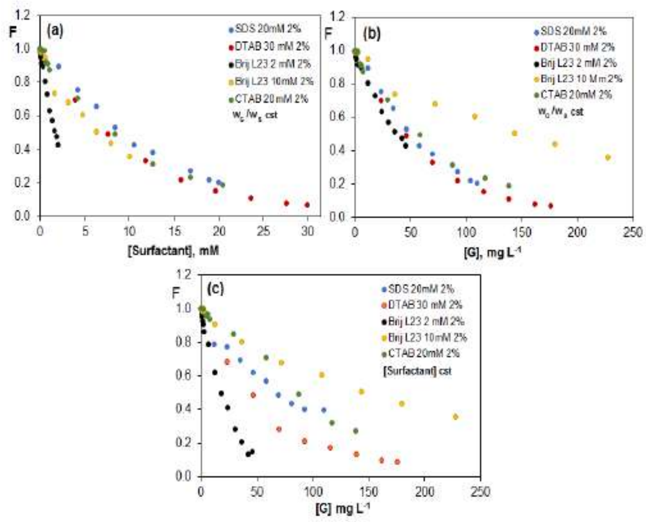

Figure 1: Fluorescence of vitamin B_2 in G 2.0 wt% dispersions in the surfactants vs. concentration of surfactants (a)and vs. G concentration for w_G/w_S =cst (b)and [surfactant]=cst (c)

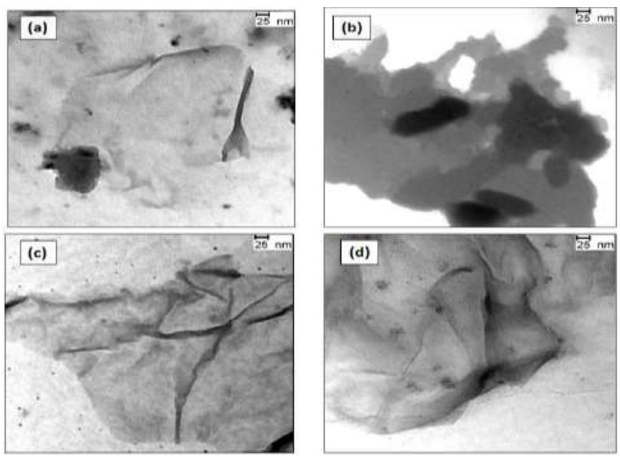

Figure 2: TEM images of G (2.0 wt%) dispersions in 20 mM SDS (a), 30 mM CTAB (b) and DTAB (c) as well as 10 mM Brij L23 (d)

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Magnetic properties of thermally oxidized Co patterns

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When a ferromagnet (FM) in close contact with an antiferromagnet (AFM) is field cooled through the Néel temperature of the AFM, the magnetic phenomenon of exchange bias arises. Thus, a shift in the FM hysteresis loop is obtained. Although this phenomenon is of technological importance and has been intensively studied, a complete understanding is still missing. Furthermore, when reducing the physical dimensions of the system to the magnetic length scale new features can arise.

We report a magnetic study of CoO/Co system with two dimensions in the nanometer scale, thickness and width.

A resist template of lines was fabricated by interference lithography on a Si wafer. Then, a Co thin film with a thickness of 20 nm was deposited by thermal evaporation. After the lift-off of the resist, lines of Co of width 400 nm and periodicity of 1000 nm were obtained (Figure 1). Co lines were thermally oxidized in air flow conditions in order to produce a thin layer of CoO.

Magnetic properties of CoO/Co (AFM/FM) lines were investigated using a SQUID magnetometer. cooling below the Néel temperature, T_N, from room temperature with an applied field.

The patterned system shows exchange bias at low temperature. The lower the temperature the higher the exchange bias field. Above 210 K, the exchange bias disappears. This is in good agreement with the blocking temperature observed in CoO/Co films.

CoO/Co lines also present 'training effect', i.e. the exchange bias field decreases as the hysteresis loop is measured repeatedly at a fixed temperature.
Although above the blocking temperature no exchange bias appears, a strong dependence of coercivity with temperature is observed. The dependence in CoO/Co lines is in contrast with previous reported results of CoO/FM films, in which the coercive field decreases with increasing temperature. [1]

In summary, we observed magnetic coupling effects in thermally oxidized Co patterns of lines. Exchange bias and training effects arise below 210 K whilst coercivity shows an unusual dependence above this temperature.

Work supported by AEI-MINECO FIS2016-76058, UE FEDER "Una manera de hacer Europa", AEI-MINECO FIS2013-45469 and the European Union FP7-IRSES-2012 Project No. 318901

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Figures

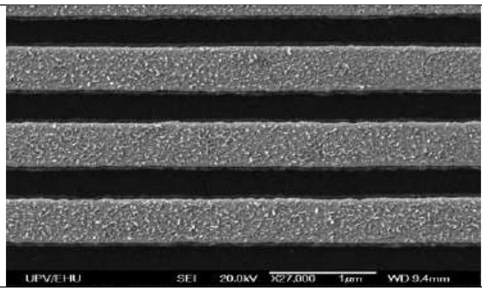

Figure 1: SEM image of the CoO/Co lines with a width of 560 nm and periodicity of 960 nm.

Versatile silica nanoparticle coating for intracellular and *in vivo* targeting analysis

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Particle selective accumulation in target tissues is pivotal in nanomedicine to improve treatment efficacy while reducing the undesired toxic side-effects. Unfortunately, identifying the location of the NPs after administration in cells or in animal models can be challenging. Silica coating represents a useful strategy to overcome these difficulties, and shows high biocompatibility, optical transparency and strong chemical and colloidal stability [1]. In addition, this surface modification improves nanoparticle dispersion in aqueous media, reducing aggregation that often limits the use of many materials in biomedicine. Furthermore, silica coating can be easily labeled with fluorophores [2], or modified with a wide variety of ligands like proteins, drugs, or other nanomaterials such as carbon nanotubes [3].
Here we present a method that allows the coating of different nanoparticles with an organic fluorescent dye embedded in a silica shell. This labelled-coating allows the tracking of non-luminescent nanoparticles intracellularly, while maintaining the innate properties of the nanomaterials that make them suitable for subsequent therapeutic applications. This method opens the possibility to design multifunctional nanomaterials with different and complementary properties.

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Figures

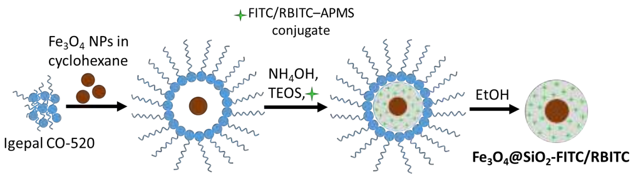

Figure 1: Steps for fluorescent silica coating of hydrophobic magnetite nanoparticles

Exploring the photo-catalytic properties of Nb_2O_5 nanoparticles synthesized by different procedures

Presenting Author (J.A. Navío)
Co-Authors (F.J.Sánchez-Fernández
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Abstract

Niobium-containing materials have been prominent in recent decades because of their special applications in the high technology industries, especially in the aerospace, metal super alloy and electro-electronics sectors. The properties of Nb_2O_5 strongly depends on its synthesis procedure as well as on the conditions of ulterior thermal treatment [1]. We report the synthesis of Nb_2O_5 powders prepared by the sol-gel precipitation method using niobium(V) ethoxide as precursor. Two chemical routes were chosen: the presence of tryethyl amine (TEA) as precipitant/template agent, or the oxidant peroxide method. Microwave-assisted activation (MW) was also used. Portions of Nb_2O_5 powders synthesized by the above procedures were amorphous. Structural changes upon heating from room temperature up to 800°C were investigated by XRD technique combined with thermo-gravimetric analysis. The sequential thermal treatment up to 800°C promotes the crystallization of hexagonal phase to orthorhombic phase whereas the ulterior cooling to room temperature lead to a mixture of both phases. Samples calcined at selected temperatures of either 600°C or 800°C for 2 h, were characterized by a wide variety of techniques. The synthetic procedure as well as the combined MW-activation followed by ulterior thermal treatment lead to changes not only on particle size but also on the textural properties of the catalysts. The photo-activity of the synthesized catalysts has been evaluated using Rhodamine B (RhB) as a substrate, under both UV and visible lighting conditions. None of the catalysts synthesized showed activity in the visible. Under UV illumination, some of the catalysts exhibited a relatively low photo-activity in the degradation of RhB, which is associated with a photosensitizing effect. However, the addition of Ag^+ ions considerably increased the activity of all the catalysts implementing considerably the degradation of RhB under UV-illumination leading to a new silver metallized sample.

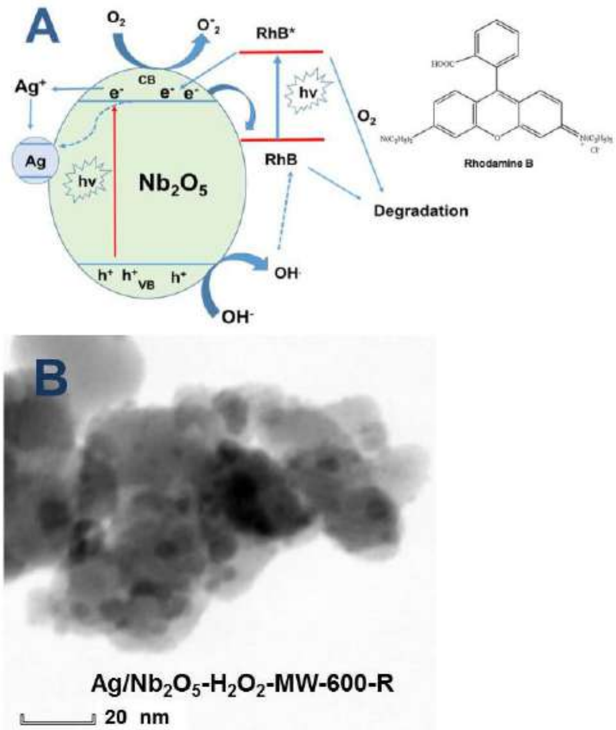

Figure 1: (A) A proposal of the degradation mechanism of RhB in the presence of Nb_2O_5 under UV-lighting conditions. **(B)** Selected TEM for the indicated sample.

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Improvement of NIR photophysical properties of a hemicyanine dye by its encapsulation within 1D-AlPO nanochannels

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Active fluorescent dyes based on small organic molecules in the near-infrared (NIR) region have awakened the interest for biomedical applications owing to minimize background interference and improve tissue depth penetration [1]. However, there are only a few dyes on the market representing this phenomenon. Thereupon, the design and synthesis of new advanced optic hybrid materials is currently a burning survey towards obtaining promising materials with enhanced properties [2]. In this work, the "one-pot" synthesis, based on the "in situ" encapsulation via crystallization inclusion method of the hemicyanine dye LDS 730 dye into 1D nanochannels of MgAPO-5 aluminophosphate, has led to a favourable bathochromic shift into the NIR spectra. The tight fitting between the molecular size of the guest dye and the pore dimensions of the host have enabled a rigid planar conformation of the Styril dye within the nanochannels [3]. Consequently, a boosted fluorescence in the NIR range of the spectra is enhanced during the occlusion with respect to the dye in solution together with an alignment among the channels. Therefore, a new hybrid material for the development of interesting potential optical properties and biomedical applications was achieved.

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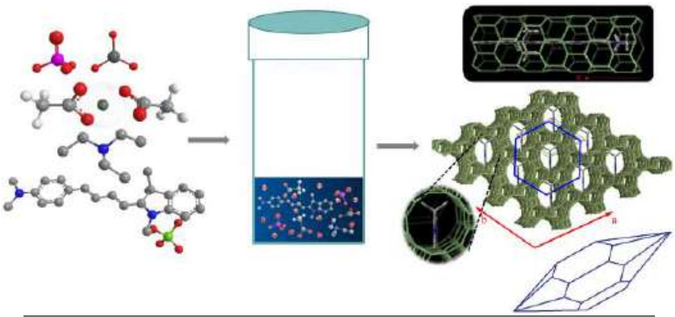

Figures

Figure 1: Hydrothermal synthesis of the red emitting LDS 730/AFI hybrid materials via microwave. The dye is embedded and confined in the zeolite matrix during the crystal growth.

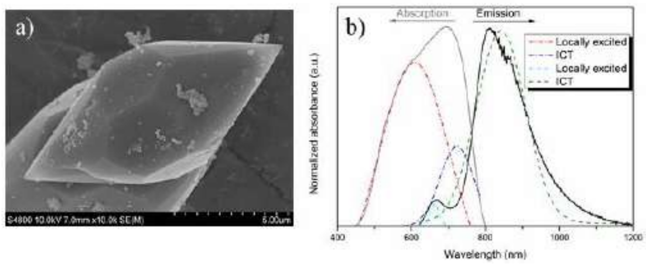

Figure 2: Molecular structure of the red-emitting LDS 730 dye with its respective dimensions calculated by optimizing the ground geometry using B3LYP hybrid functional (DFT) via Gaussian 09. B) The structure of AFI, MgAPO-5 aluminophosphate.

An amperometric biosensor for determination of heavy metal ions, based on a Thiolated DAB dendrimer to form self-assembled monolayers with Gold nanoparticles and HRP.

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Beatriz Alonso[2]
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Heavy metals such as lead, copper, cadmium and mercury have been implicated in soil, air and water contaminations. These heavy metals 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]. 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 [2]. Furthermore, the AuNPs present a high biocompatibility with the enzyme Horseradish peroxidase (HRP) maintaining their bioactivity [3]. Here we present a new amperometric hydrogen peroxide (H2O2) biosensor developed by immobilizing (HRP) onto colloidal gold nanoparticles (AuNPs), covalently bonded to a third generation thiolated DAB dendrimer linked in turn to a glassy carbon electrode (GCE) via electro-generated gold nanoparticles forming self-assembled monolayers (SAMs). The new biosensor show direct electrochemistry with the HRP and have been applied to the indirect determination of Pb2+ based on the inhibition of HRP. The inhibition measurements have used by other authors o develop several heavy metals sensors [4]. The inhibition by Pb allow us to have a highly effective biosensor, with sensitivity 0.6709 µA µM^{-1} cm^{-2}. In addition, the obtained apparent Michaelis-Menten constant, $K_{M,app}$, was 0.05 mM, significantly lower than the intrinsic KM, reveling the very high enzymatic efficiency of the developed device. Tis work is being extended to other heavy metals as copper, cadmium and mercury.

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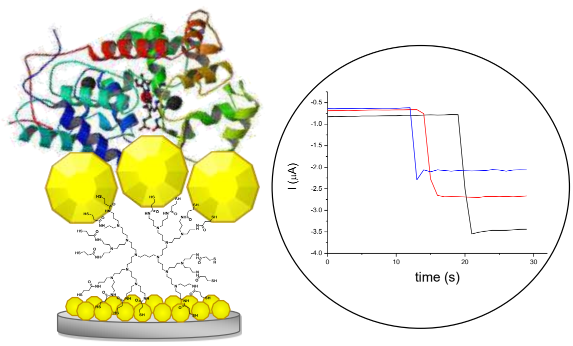

Figure 1: Scheme of biosensor and their response in absence (black) and presence of lead 0.05 mg L^{-1} (red) and 0.1 mg L^{-1} (blue).

Magneto-catalytic graphene quantum dots Janus micromotors for bacterial endotoxin detection

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Magneto-catalytic hybrid Janus micromotors encapsulating phenylboronic acid (PABA) graphene quantum dots (GQDs) are used here as ultrafast sensors for detection of deadly bacteria endotoxins. A bottom-up approach is adopted to synthetize an oil-in-water emulsion containing the GQDs along with a high loading of platinum and iron oxide nanoparticles on one side of the Janus micromotor body. The two different "active regions" allow for highly efficient propulsion in the presence of peroxide solutions or magnetic actuation. Fluorescence quenching is observed upon GQDs interaction with the target endotoxin (LPS), with the PABA tags acting as highly specific recognition receptors of the LPS-core polysaccharide region. Such adaptive hybrid operation and highly specific detection hold considerable promise towards diverse clinical, agro-food and biological applications with clear promising to integrate in future lab-on-chip technology.

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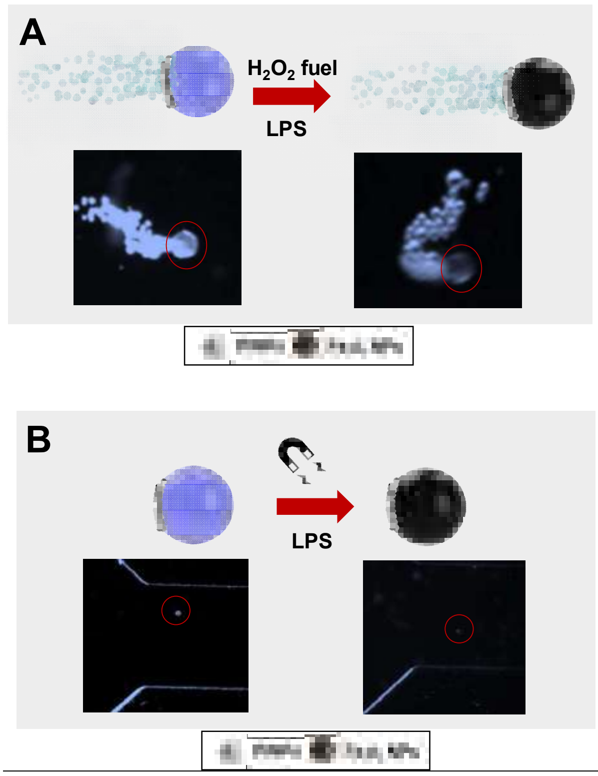

Figure 1: *Bubble-propulsion and optical microscopy images of the Janus micromotors before and after LPS addition. (B) Optical microscopy images of the magnetotactic behaviour the Janus during its navigation in the different channels of a PDMS chip. Scale bars, 20 µm.*

Open-atmosphere laser nanostructuring of silicon using a laser-induced plasma lens

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Nanostructuring of a metal surface by means of laser irradiation is an area of primary interest in nanotechnology. There is a recent trend to use these type of targets for X-ray generation, ion acceleration and the study of intense plasmonics in high intensity laser-matter interaction. Many studies have been carried on the formation of more or less ordered, or periodic, nanostructures when a metal or semiconductor substrate is irradiated with pulsed laser light. Such structures have been obtained with techniques based on laser scanning microscopes with ultra-short laser pulses by a two beam irradiation of a silicon surface achieved using a Lloyd mirror configuration or by the interference between two or more laser beams.
However, the physics behind is not fully understood. So far, none of the mechanisms proposed can fully explain these results, the most accepted mechanism involving the excitation of the semiconductor surface plasmon by the incident laser light. This would occur on the molten surface layer where the free electrons can support the propagation of surface plasmons. The surface would adopt a grating-like shape depending on the relation between the wave-vector of incident laser light and the surface plasmon and its rapid cooling after the laser pulse would retain such morphology.
In this work, we propose a simple plasma lens technique for obtaining a multiple nanostructuring effect without the need of femtosecond laser sources nor a controlled environment. A laser-induced plasma is used as a non-linear optical element for a second laser beam which crosses the plasma perpendicularly to its expansion axis. By varying the time delay between the two lasers beams, and the fluence of the laser generating the plasma plume, various patterns were induced on the surface of the silicon wafers used.

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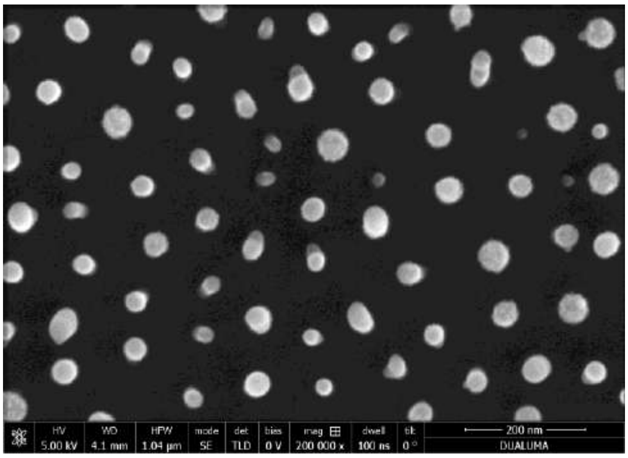

Figure 1: SEM image of a silicon sample showing one of the structures produced by the technique presented in this work.

Self-organized dynamic ultradisperse structures on the interface in two-dimensional open system with first-order phase transition.

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The phenomenon of periodic crystallization and melting of the surface layer of a system in isothermal conditions at a temperature close to the phase transition temperature is studied.
The system is a dilute solution of a volatile admixture (NH_3 or C_2H_5OH) in water and consists of microspheres of the solid phase of the solvent (H_2O) distributed in the surface layer of the solution; they aggregate with each other and form a two-dimensional disperse system.
The dimensions of the nuclei of the solid phase during their evolution vary from 0.1 to 10 microns.
The system is open: the admixture diffuses into the system from the reservoir and evaporates from the surface. In a known range of parameters and boundary conditions, dissipative structures arise in the system, as well as autowaves of structural rearrangement.
It is established that the solidification wave front is a traveling fractal cluster, the melting wave is also scale-invariant.
The variety of dynamic regimes of the system is caused by the presence of metastable states under the cooperative interaction of its elements and the influence of surface effects.
Mathematical models of the phenomenon are proposed, investigated and discussed. There is every reason to believe that such phenomena can be detected in ultradispersed systems at both micro- and nano-scales.

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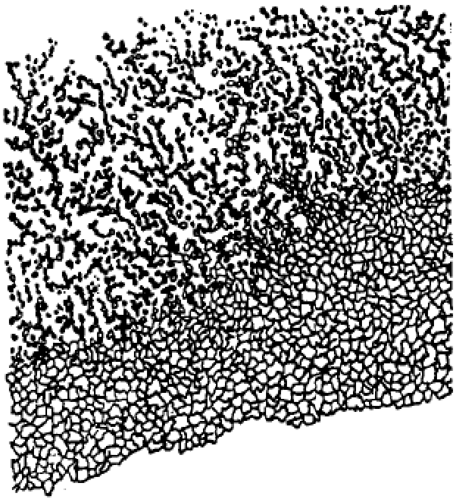

Figure 1: The solidification wave front is a traveling fractal cluster of aggregated microspheres of the solid phase of the solvent (H_2O) distributed in the surface layer of the solution. The dimensions of the nuclei of the solid phase during their evolution vary from 0.1 to 10 microns. The motion of the crystallization front is directed from the bottom to the top.

Safety Delivery of Camptothecin: From Prodrugs to Nanomedicines

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Introduction. 20-(S)-camptothecin (CPT) is a natural planar pentacyclic quinolone (Fig. 1) with strong antitumor activity against a wide spectrum of human cancers.[1] Unfortunately, CPT presents some major limitations with regards to therapeutic application, like poor water solubility and the rapid lactone ring hydrolysis at physiological pH, which gives rise to the inactive carboxylate form.[2] In addition, CPT is extremely insoluble in biocompatible solvents, which makes impossible conventional administration routes. To overcome these issues two strategies have been pointed out: i) structural analogues, in which the CPT molecule is chemically modified for increased solubility and stability in biological fluids; and ii) nanomedicines, wherein CPT is incorporated by physico-chemical methods to nanoparticles which act as stable carriers for drug delivery. We here present some of the most advanced and recent achievements in the design, synthesis and development of CPT analogues and nanomedicines.

Results. Most structural derivatives of CPT have been obtained through modifications of the quinolone A-B ring [1]. This include substitution at C9, C10 or C11 by amine or hydroxyl group, to give compounds with more antitumoral activity, whereas substitution of positions 9 and 10 by halides or other electron-rich groups and substitution of position 11 with fluorine or cyano groups increase the DNA topo I inhibition ability. Conversely, modification of the E-ring, mostly at C20 position, increases lactone stability. On the other hand, CPT nanoplatforms present major advantages as improved solubility, lactone ring stability, half-life extension, biocompatibility and control drug release rates.[3] Some of the most successful systems we have tested in preclinical research are: (i) fully inorganic core-shell nanoparticles obtained by coating gold nanoclusters with a mesoporous silica layer; (ii) redox sensitive derivatives of CPT coupled by disulfide bridge over complex silica nanoparticles containing a non-porous core and a mesoporous shell; and (iii) hybrid organic-inorganic silica nanoplatform with CPT linked by ester bond.

Discussion. Therapies merely relying on single, small molecules seem now out of step, due to their limited efficacy and unacceptable toxicities. For this reason, future seems good for those systems which are able to selectively discharge CPT at the target cells under a specific stimulus (stimuli-responsive), with no previous release.

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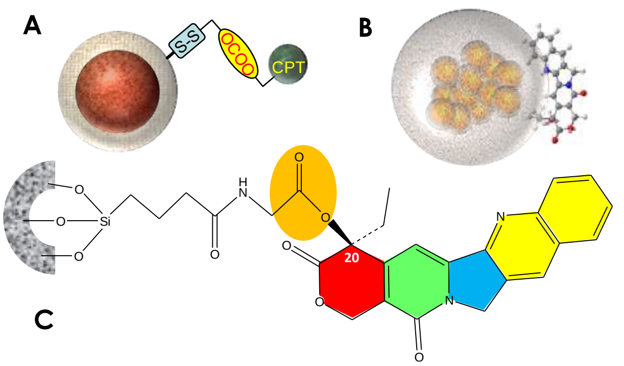

Figure 1: (A) Core-shell nanoparticles of gold nanoclusters coated with a mesoporous silica layer with CPT. (B) Redox sensitive derivative of CPT coupled by disulfide bridge dense core-porous shell silica nanoparticles; (C) Organic-inorganic silica nanoplatform with CPT linked by ester bond.

Synthesis of cerium oxide nanoparticles for medical applications

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Metal oxide nanoparticles are one of the most promising materials for applications in biotechnology because of their interesting properties at nanoscale. In particular, cerium oxide nanoparticles (CeO_2 NPs) have special interest in medicine due to their catalytic activity as antioxidant agent, being able to scavenge reactive oxygen species (ROS) such as H_2O_2, OH. , O_2-[1,2]. For that reason, a proper synthesis of this material is necessary and characteristics of CeO_2 NPs produced have to be evaluated before their utilization. On the other hand, CeO_2 NPs will interact with proteins both in culture media and blood torrent, especially with albumin, forming a protein-corona structure[3]. Thus, a study of conjugated CeO_2-Albumin is also required to predict their behavior in physiological media. In conclusion, synthesis of CeO_2 NPs will be responsible for characteristics of material so, studying and developing this process will be essential for taking the maximum advantage of their desired properties from cerium oxide nanoparticles for future medical applications.

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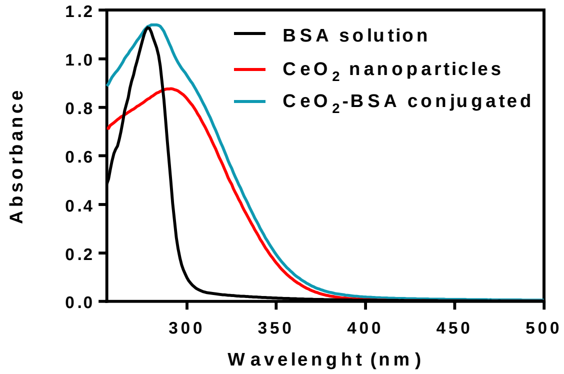

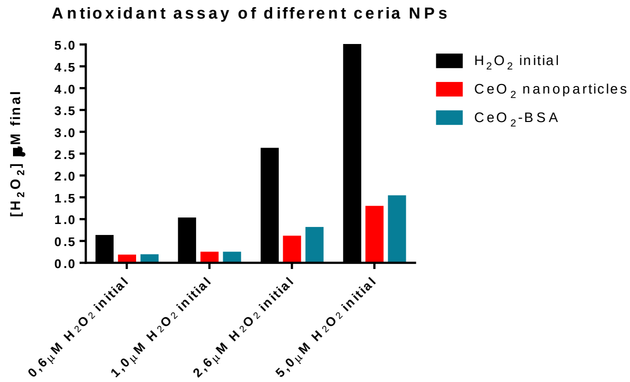

Figure 1: In the left, ultraviolet spectres of ceria nanoparticles and their conjugation with Albumin. In the right, Antioxidant assay of ceria nanoparticles and their albumin-conjugated measured by Amplex Red technique

MWCNT scaffold films for total α_1- acid glycoprotein determination in serum samples

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Abstract

Alpha-1-acid glycoprotein (AGP) or Orosomucoid is a serum glycoprotein with a molecular weight between 41-43 KDa [1]. Total AGP content has been studied as serum biomarker for inflammatory bowel diseases [2]. In this sense, there is a need for developing fast and cheap analytical methods for diagnosis, prognosis and follow-up of these diseases.
We propose a simple and cheap electrochemical method for total AGP determination using disposable multiwalled carbon nanotube scaffold films (MWSFs).
The fabrication of these electrodes relies on the filtration of a homogeneous dispersion of the carbon nanomaterial on the Teflon filter which becomes the scaffold for the nanomaterial assembling without the need of any high external pressure, energy or growing chemistry. MWSFs present several distinct advantages when compared to traditional composites: casting or direct nanomaterial growing, straightforward and reproducible preparation, versatility, and exceptional conductivity at the micro and sub-micron levels [3].
To achieve the electrochemical detection of AGP, the protein was labeled with an osmium (VI) complex (see Fig 1). Analytical performance of MWSFs electrodes were compared with commercial carbon screen printed electrodes (SPE). Lower limits of detection and higher fouling resistance were displayed by MWSFs. Finally, the developed method was successfully applied to serum samples demonstrating that it could be useful in clinical diagnosis.

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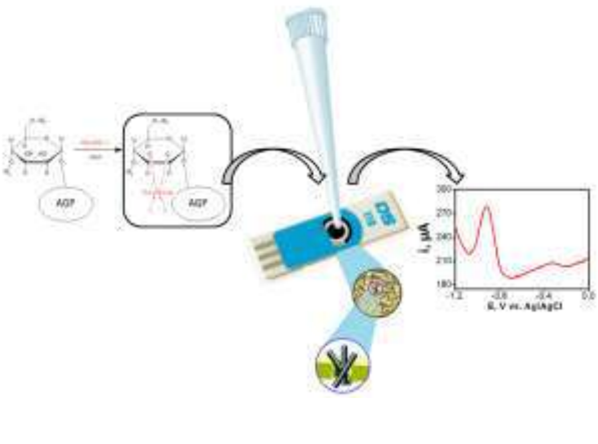

Figure 1: Process to carry out the measurements of α_1- acid glycoprotein using MWCNT scaffold films.

Influence of magnetron sputtering parameters on the properties of GIZO thin films

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Gallium Indium Zinc Oxide (GIZO) has emerged as a high quality transparent conductive oxide (TCO) due to its high transmittance, conductivity, mobility, low temperature growth and suitability for many types of substrate materials[1]. Amorphous and crystalline GIZO were obtained by RF-magnetron co-sputtering on glass, employing In_2O_3 (99.99%) and 2% Ga-doped ZnO targets. A Box-Behnken experimental design was used with three different deposition time (20, 40 and 60 minutes), substrate temperature (150, 250 and 350 °C) and RF-power levels of In_2O_3 (80, 110, 140 W). The influence of these three parameters on the properties of GIZO thin films were observed being the In_2O_3 RF-power the most significant effect that improve the conductivity of the films. The best results of electrical conductivity were found for an amorphous GIZO with a value of 1.67E+03 $\Omega^{-1}\cdot cm^{-1}$.

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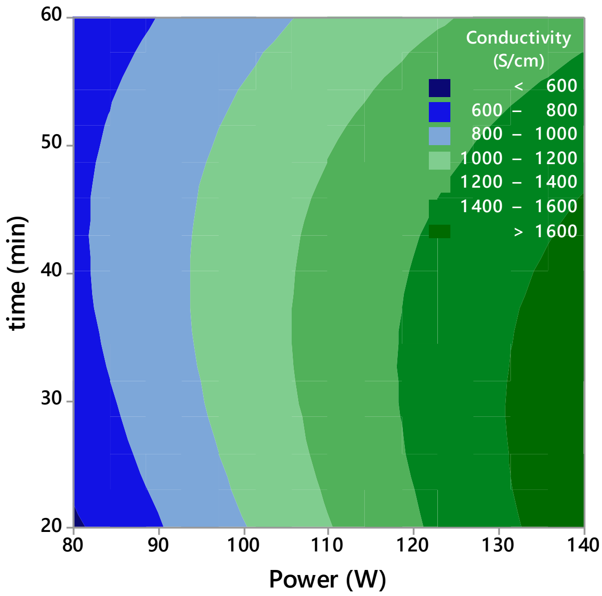

Figure 1: Contour graphs of GIZO thin film conductivity as a function of Power and time.

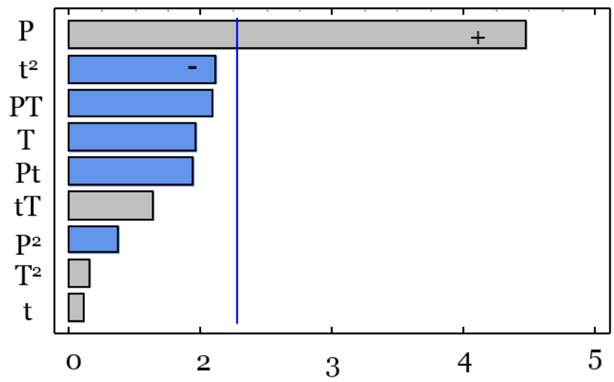

Figure 2: Pareto graph of the standardized effects over IGZO thin films.

GRAPHIN2018 – SPEAKERS

Innovative solid sorbents based on modified graphene and MOF materials for CO2 capture

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Global warming resulting from the emission of greenhouse gases has received widespread attention with international action from governments and industries, including a number of collaborative programs, such as SET-Plan, and very recently the International Climate Change hold 2015 in Paris . Key European Commission roadmaps towards 2030 and 2050 have identified Carbon Capture and Storage (CCS) as a central low-carbon technology to achieve the EU's 2050 Greenhouse Gas (GHG) emission reduction objectives, although there still remains a great deal to be done in terms of embedding CCS in future policy frameworks. CO2 capture process represents typically about 70% of the total cost of the CCS chain, and therefore, novel adsorption technologies that can offer various advantages over conventional adsorption, such as high operating flexibility and low maintenance costs, are gaining support nowadays. One of the most promising technologies for CO2 capture is based on the adsorption process using solid sorbents, with the most important advantage being the energy penalty reduction during capture and regeneration of the material compared to liquid absorption.

GRAMOFON aims to improve the selectivity and efficiency of the dry sorption process-physical adsorbents- for post-combustion CO2 capture, taking into account several active material structures, such as, shaped Metal-Organic Frameworks (MOFs), amine functionalized graphene oxide aerogel (meso- and microporous structures), and shaped MOFs/functionalized graphene oxide composites.

The GRAMOFON project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement nO 727619. The sole responsibility for the content of this presentation lies with the GRAMOFON project and in no way reflects the views of the European Union.

Non-contact conductivity mapping of graphene: setting new standards

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The significant progress in fabricating large-area graphene films for transparent electrodes, barriers, electronics, telecommunication and other applications dictates the development of large-area characterisation and quality control. Conventional methods for electrical mapping are often slow, destructive, unreliable or combinations of these.

I will briefly review and compare three different, but complementary approaches that all have been optimized for throughput, accuracy and minimal damage to the graphene. These include (1) fixed contacts using dry laser lithography, (2) movable contacts using micro four point probe, and (3) THz time domain spectroscopy (THz-TDS), which analyses the electrical properties from the absorption of terahertz pulses.

The main emphasis will be on THz-TDS, which is non-destructive, highly accurate and allows both conductivity, carrier density and carrier mobility to be mapped across arbitrarily large areas at rates that by far exceed any other known method. Moreover, I will show how the THz conductivity spectra reveals hidden information on the carrier scattering dynamics which are subject to growth, transfer and processing conditions. This is highlighted through insights from recent collaborative projects. The ongoing efforts to turn THz-TDS into a metrology standard, and to upscale the method will be discussed.

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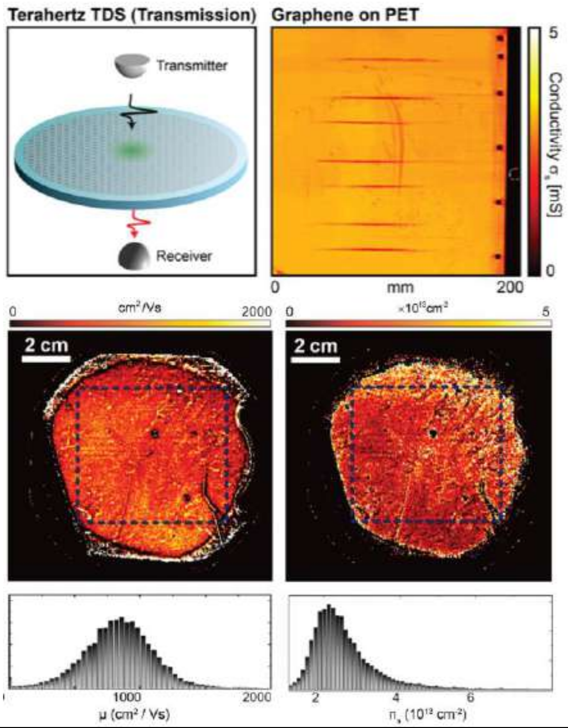

Figure 1: Top: illustration of THz-TDS setup, with a conductivity map of a 200x200 mm graphene sheet on PET polymer. Bottom: carrier mobility (left) and density (right) of 4'' graphene sheet.

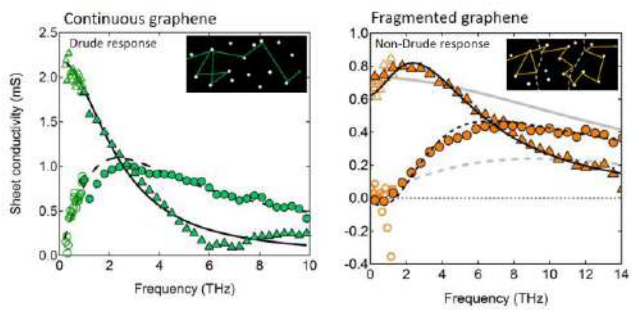

Figure 2: Comparison of THz-TDS conductivity spectra from continuous high quality graphene (left) and discontinuous graphene with line-defects.

Scaling up prospective for the production of graphene and other 2D crystals

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We propose liquid-phase exfoliation of layered materials [1,2] as a simple and cost-effective pathway to fabricate various two-dimensional (2D) crystals. We exploit solution processed 2D crystals for the designand realization of (opto)electronic and energy devices, presenting huge integration flexibility compared to conventional ones.[1-6] However, a key requirement for the realization of such applications is the development of industrial-scale, reliable, cost-effective production processes,[2] while providing a balance between ease of fabrication and final material quality with on-demand properties. Here, I will show our scaling up approach for the solution processing of 2D crystal based on wet-jet milling of layered materials. Moreover, I will present an overview of 2D crystals for flexible and printed (opto)electronic and energy applications, from the fabrication of large area electrodes[3] to devices integration.[6-13]

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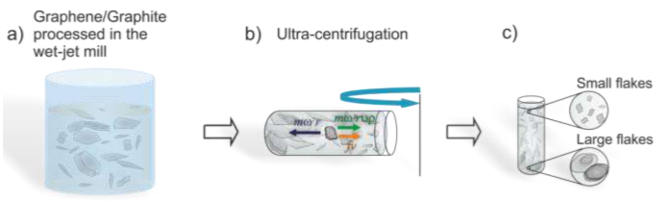

Figure 1: (a) Purification of the wet-jet milled graphite carried out by (b) sedimentation based separation, applying a centrifugal force to sort the flakes according with their morphological properties. (c) This procedure allows the thinner and smaller flakes enriching the supernatant, while the large or un-exfoliated flakes sediment at the bottom of the centrifuge tube.

Graphene and related materials deposition by spray-gun deposition method. A versatile technique for a large panel of applications.

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Abstract

Spray-gun deposition method is an extremely versatile method that can be exploited using different materials and substrate. At Thales Research and Technology we have developed a new technique that allows depositing nanomaterials mixtures for different applications. Firstly in 2006, we developed this method to fabricate array of Carbon Nanotubes (CNTs) based transistors for gas sensing applications. We were able to achieve extremely thin layers of percolating CNTs to achieve the transistors channel of Carbon Nanotubes Field Effect Transistors (CNTFETs). In 2012 we started developing this method using mixtures of graphene and CNTs for supercapacitors fabrication. Indeed thanks to this technique we discovered that we were able to achieve nanostructured layers that can allows exploiting at maximum the graphene surface to store more energy but also to define a porous structure particularly effective to improve the power. In 2014 we also thought to implement this technique to deposit large area layer of Graphene Oxide (GO) to fabricate ReRAM, exploiting the migration of oxygen vacancies in the GO layer after applying a bias between a bottom and top contacts. The great advantage of spray in this case is that we can implement the technique by roll-to-roll and therefore achieve large surface on also plastic substrates, reducing dramatically the final price. Recently, we want to implement this technique for Electromagnetic Shielding. Indeed thanks to graphene layer deposited by spray we can achieve multi-layered structures in a quite deterministic way enhancing the absorption to specific frequencies in the X-band.

During the presentation all the different applications and the versatility of this technique will be highlighted .

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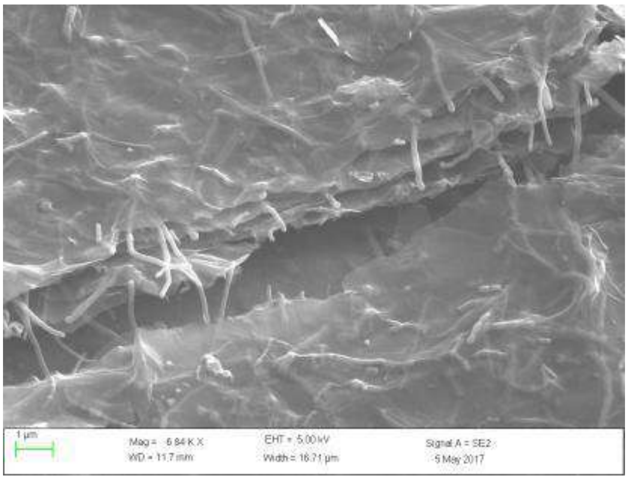

Figure 1: Multi-layered structure obtained intercalating Carbon Nanofibers and Graphene by spray deposition method.

2D Materials: science and technology

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I will review the last developments in the science and technology of 2D materials

Organic 2D Materials: Grand Challenges and Opportunities

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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 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 exploration of graphene and inorganic 2D crystals such as metal dichalcogenides, boron nitride, black phosphorus, metal oxides and nitrides, the study on organic 2D crystal systems including the bottom-up organic synthesis of graphene, 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 synthetic approaches towards novel 2D organic materials with structural control at the atomic/molecular-level or at the meso-scale. First, we will present the solution synthesis of 2D sp2-carbon based conjugated polymer frameworks as the new generation covalent-organic frameworks. Second, we will introduce the latest development on the synthetic 2D conjugated polymers including 2D Schiff-base type covalent polymers and 2D metal-dithienene/diamine coordination supramolecular polymers at the air-water or liquid-liquid interfaces. The resulting 2D conjugated polymers exhibit single-layer feature, good local structural ordering and with a size of cm^2. The functional exploration of such 2D single-layer conjugated polymers for the electrical and mechanical properties, as well as serving as efficient electrocatalytic water splitting catalysts will be demonstrated. Third, we will introduce the self-assembly of a host-guest enhanced donor-acceptor interaction, consisting of a tris(methoxynaphthyl)-substituted truxene spacer, and a naphthalene diimide substituted with N-methyl viologenyl moieties as donor and acceptor monomers, respectively, in combination with cucurbit[8]uril as host monomer toward monolayers of an unprecedented 2D supramolecular polymers at liquid-liquid interface. Finally, we will present the supramolecular approaches to synergetic control the multi-component assembly, which results into 2D conducting polymers, such as polypyrrole and polyaniline nanosheets featuring 2D structures and with adjustable mesopores with/without on various functional free-standing surfaces. The unique structure with adjustable pore sizes (5–20 nm) and thickness (35–45 nm), enlarged specific surface area as well as high electrical conductivity make 2D conducting polymers promising for a number of applications. The future perspective and outlook regarding the goal towards highly crystalline organic 2D materials will be provided.

Hybrid 3D graphene materials for energy applications

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Three-dimensional graphene based materials are of great interest as they combine the intrinsic properties of graphene, with high specific surface area and low density. In this work we present a novel, simple and versatile method to synthesize materials based on 3D graphene with supported metal oxide nanoparticles (3D-rGO/MOx) by a hydrothermal process. The synthesis process combines the growth of metal oxides nanoparticles and the reduction of GO in one single step, followed by a freeze drying treatment.

The obtained 3D-rGO/MOx materials exhibit inherent properties like a microporous/ mesoporous structure of graphene sheets with homogenous dispersion of MOx nanoparticles, large surface area and large pore size distribution. It allows easier access and fast transport of the electrolyte solution to the adsorption sites, high specific capacitance, high electrical conductivity; and superior electrochemical stability comparing with other carbonaceous materials such as activated carbons.

As a prove of the versatility of this 3D-rGO/MOx material, we present the preparation of electrodes for water deionization and cathodes for lithium-sulfur batteries [1].

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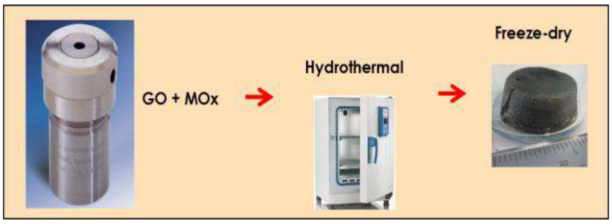

Figure 1: Hydrothermal method to synthesize 3D-rGO/MOx materials

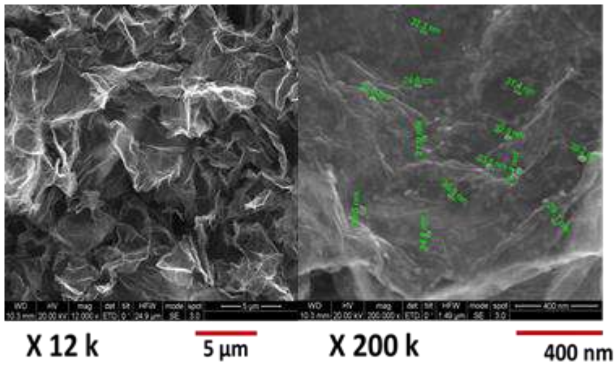

Figure 2: SEM images of 3D-rGO/Fe_2O_3

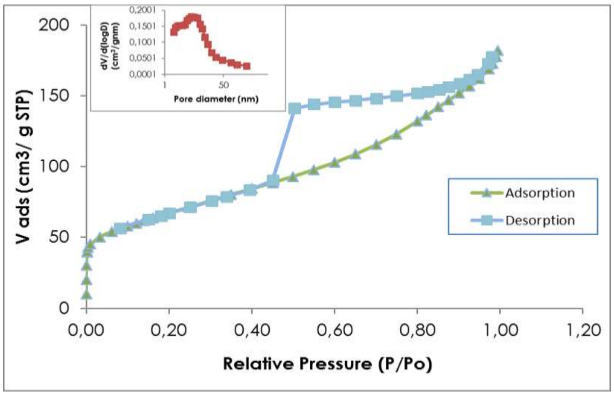

Figure 3: N_2 adsorption-desorption isotherms and pore size distribution (inset) of 3D-rGO/Fe_2O_3

Relevance of an adequate of selection of the graphene materials and processing conditions in the preparation of GRM composites

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The bulk graphene materials market will grow to 350 € million in 2025. Their application in composites is the largest segment, followed by energy storage [1]. Several reviews analysed the applications of the different graphene and related products in composites.[2, 1b]
Graphene materials (GRM) are a big family of materials with remarkable differences in morphology, dimensions, aspect ratio, surface chemistry, etc. An adequate selection of the GRM and processing technique is a key factor for achieve the desired properties. Also and adequate nomenclature and standardised or industrial accepted characterization techniques are needed for the application and avoid lost of efforts and resources.
In this presentation we will compare the influence of the various graphene materials prepared by different methodologies, from LPE to oxidation/reduction, with variations in lateral size, dimension and surface chemistry and processing technologies for the preparation of composites in the final properties of the composites.

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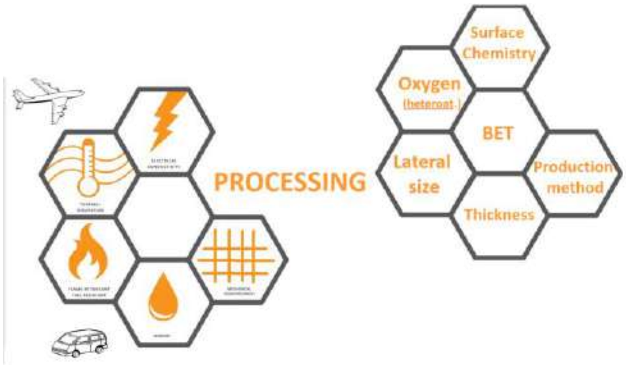

Figure 1: . Scheme of GRM characteristics vs properties

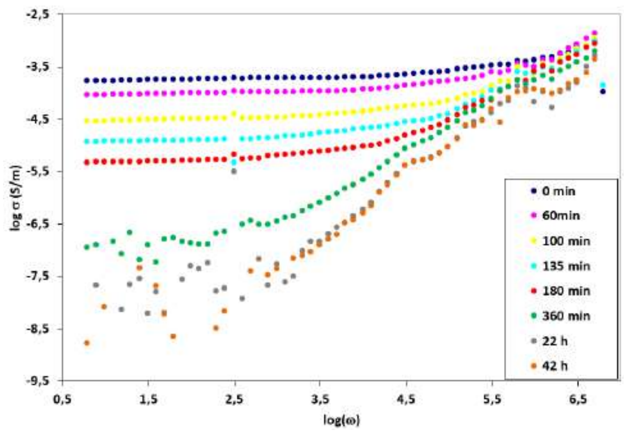

Figure 2: Monitorization of a.c. conductivity during the polymerization of a GRM-epoxy composite

Graphene Nanofluids- From Thermal to Electrochemical Applications

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Graphene is the advanced material of choice for a wealth of applications, but it has customarily been used as a solid. Yet, fluids are key materials for a variety of industrial applications, from thermal to electrochemical devices.

Graphene Nanofluids, formed by graphene nanosheets dispersed in suitable base fluids can be prepared as stable dispersions in organic or aqueous solvents [1] and they show most interesting thermal and electrochemical properties.

Thus, for the field of thermal energy conversion and storage, we have developed stable graphene nanofluids of different concentrations in suitable organic solvents as base fluids (dimethylacetamide /dimethylformamide) and have shown their enhanced thermal conductivity (Figure 1) using a modified 3-ω technique adapted to liquid samples[2].

And related to electrochemical energy storage, we have developed electroactive nanofluids based on Reduced Graphene Oxide (RGO) dispersed in acidic aqueous electrolytes showing ultrafast charge transfer (Figure 2) [1]

We will present and discuss both experimental research lines with examples such as the 48% increase in thermal conductivity of our 0.18% graphene in DMAc nanofluid (Figure 1) or the capacitive response of an aqueous RGO nanofluid at the very fast scan rate of 10000 mV/s (Figure 2).

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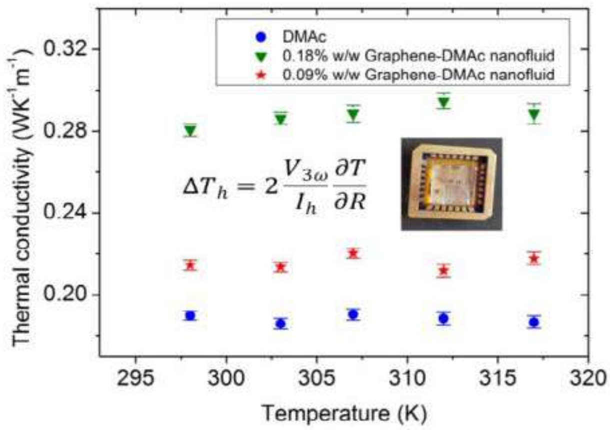

Figure 1: Strong enhancement of thermal conductivity with tiny amounts of graphene in dimethylacetamide nanofluids (up to 50% increase for the 0.18% graphene nanofluid)

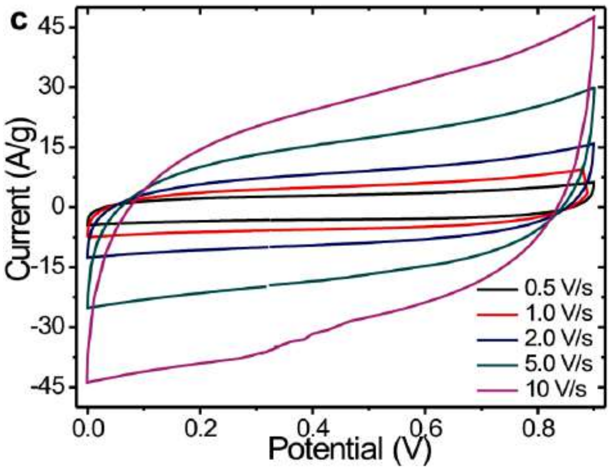

Figure 2: Cyclic voltammograms of graphene nanofluids (in this case RGO in water) showing high capacitive signals even at extremely high scan rates

Graphene as enabler for broadband image sensors integrated with CMOS and flexible platforms

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Integrated circuits based on CMOS (complementary metal-oxide semiconductors) are at the heart of the technological revolution of the past 40 years, as these have enabled compact and low cost micro-electronic circuits and imaging systems. However, the diversification of this platform into applications other than microcircuits and visible light cameras has been impeded by the difficulty to combine other semiconductors than silicon with CMOS.
We show a broadband image sensor based on the monolithic integration of a CMOS integrated circuit with graphene. [1] The graphene is covered with colloidal quantum dots to sensitize it to UV, visible and infrared light (300 – 2000 nm). [2,3] This demonstration of a broadband graphene-CMOS image sensor is a major leap towards 3d integrated circuits based on 2d materials and Si-CMOS that can perform even more complex tasks than Si-CMOS alone.
Furthermore, we will show a prototype wellness monitor based on graphene colloidal quantum dot hybrid detectors. We leveraged graphene's flexible and transparent properties to create a wearable device that is conformal to the human body so that it can extract vital signs such as heart rate, breathing rate and oxygen saturation more reliably than conventional devices.

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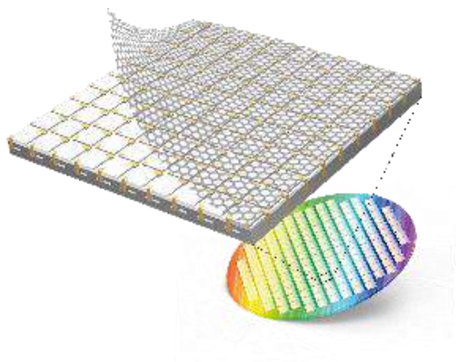

Figure 1: Artistic impression of the image sensor die coated with graphene.

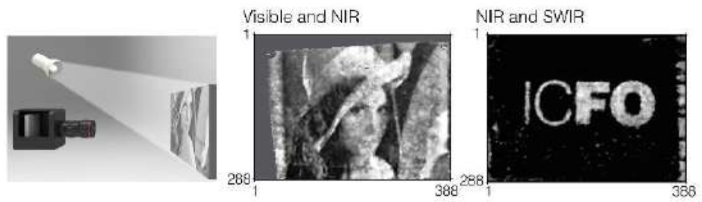

Figure 2: From left to right Digital camera setup representation, Visible light photograph of standard image reference 'Lena' and Near infrared and short wave infrared light photograph of a logo cut out of a metal sheet.

Figure 3: Photograph of the packaged image sensor.

Towards Wafer Scale Integration of CVD Graphene and 2D Materials

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Abstract

Key to commercial uptake of two-dimensional (2D) materials in electronics is the availability of scalable manufacturing and integration processes. Since a disruptive replacement of existing technology is unlikely at this point, 2D process technology should be compatible with conventional semiconductor manufacturing. While wafer scale production of graphene and 2D materials is feasible by chemical vapor deposition and related methods, the transfer of such grown layers to target substrates still faces severe challenges. In addition, defining and controlling quality, yield and reproducibility of (opto-)electronic devices is at a very early stage. This presentation will discuss approaches to graphene wafer scale integration, including yield and reliability tests of electronic devices [1], [2] and wafer scale integrated photodetectors [3]. It will also discuss device integration of the group ten material platinum diselenide ($PtSe_2$), which can be grown from thin platinum films at 400°C and below [4].

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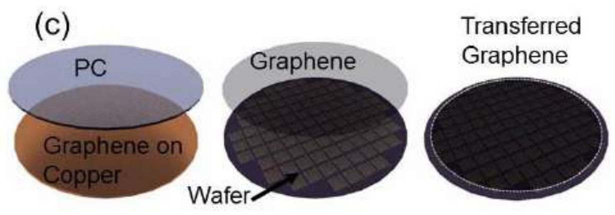

Figure 1: Wafer scale transfer of graphene (adapted from [1]).

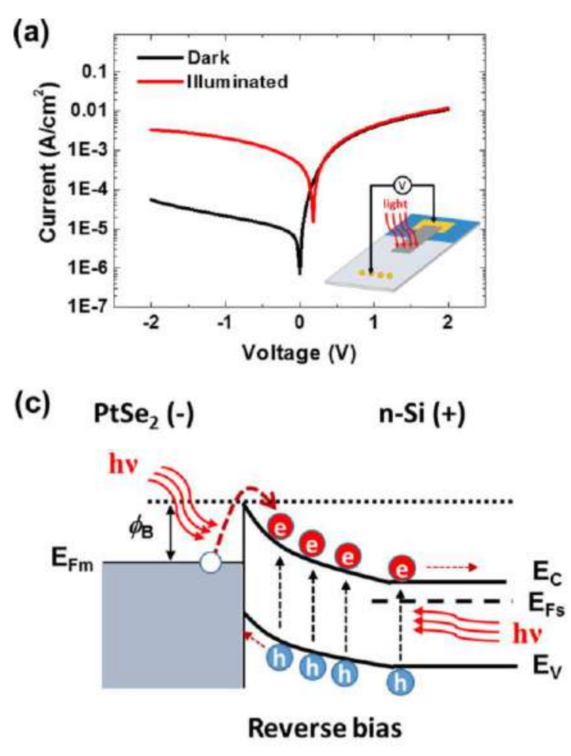

Figure 2: $PtSe_2$ – silicon Schottky diode and operation principle (adapted from [4])

Nanoreg2 SbD case study: Carbon nanofibres produced by the floating catalyst technique

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Safe by Design Grupo Antolin case study in Nanoreg2 project is based on the production of carbon nanofibres by the floating catalyst method focusing on two products GANF and GAtam and with the aim of choosing the most suitable option for the scale-up considering SbD aspects. The main differences between the two nanomaterials are the specific surface area, surface functionalization characteristics, and degree of graphitization or crystallinity.

The case study has been developed and arranged in the following tasks:

1) Risk assessment (RA) before the SbD: Selection and application of preliminary risk assessment tools at all points of the production process of both GANF and GAtam. Gaps in information and hot spots for SbD were identified in this way.

2) Design and implementation of a safer process: Different possibilities were studied in the hot spots identified in task 1 for making the production process safer. The best possibility is currently being simulated / implemented in the industry. The gaps in information identified in task 1 are being filled.

3) RA after the SbD: With the tools selected from the SIA toolbox a risk assessment is being performed after the implementation of the design to make it safer.

4) Life Cycle Analysis (LCA): The LCA is being done before and after the SbD in order to determine the improvements during all the life of the product.

5) Socioeconomic analysis (SEA). The results of both RA and LCA will feed a socioeconomic analysis where the improvements made will be measured in terms of benefits.

There are also limitations from the point of view of grouping carbon nanofilaments. Carbon nanotubes are very resilient structures extremely difficult to be shortened due to their co-cylindrical distribution of basal or graphene planes along their fibre axis. On the other hand, CNTs present a highly hydrophobic and chemically inactive surface hard to be functionalized due to the absence of basal plane edges or defects.

Any kind of carbon nanofilament with different structural arrangement of basal planes than co-cylindrical are considered CNFs. They present numerous basal plane edges and defects on their surface that favour their surface functionalization and wettability. Besides, CNFs are very sensible to physical forces applied against van der Waals bonding between basal planes leading to exfoliation phenomena and fibre shortening.

It is also necessary to consider that carbon nanofilaments grown by c-CVD techniques present a certain content of catalyst nanoparticles content as metal impurities. These metal nanoparticles play also an important role from the point of view of SbD barriers.

Standardisation of terminology and measurement for graphene and related 2D materials

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Potential innovators of real-world graphene products cannot efficiently develop new applications in the many technological areas where graphene is predicted to be disruptive, as they do not know the properties of the material supplied to them. This may be because the material has been characterised in a way that leads to large uncertainties, or because a lack of batch-to-batch reproducibility means the original characterisation is only accurate for the initial batch of material. Thus companies developing commercial products do not truly understand the effects the different properties of the material have on the final desired properties of their application.
Thus, there is a need for reliable, accurate and precise measurements for off-line material testing, which are standardised across the industry and therefore allow end-users to be able to compare materials commercially available around the world. At the same time, these accurate and precise measurement techniques and protocols are required before any reliable quality control (QC) methods can be developed for either the production of material or intermediates in the production chain. Crucially, international standardisation of the terminology and measurement methods is required so that graphene can be a truly global industry, allowing materials to be traded between producers and end-users in the many different countries currently pursuing graphene applications.
The current state of international standardisation in this area will be detailed. Importantly, the recent publication of the first ISO (International Organization for Standardization) standard, 'ISO/TS 80004-13:2017: Nanotechnologies -- Vocabulary -- Part 13: Graphene and related two-dimensional (2D) materials'[1,2] will be described, including several of the key terms and definitions.
Furthermore, the new NPL Good Practice Guide entitled 'Characterisation of the structural properties of graphene', developed in collaboration with the University of Manchester, UK, will also be explored. As well as how this guide will be the basis of new ISO measurement standards being developed to ensure the reliable, reproducible and comparable characterisation of graphene, worldwide.

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Onyx, a new standard for 2D materials characterization

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Onyx is a turnkey, non-contact and non-destructive device for the inspection of several properties of graphene and other 2D materials. Onyx generates full-area maps of conductance, resistance, thickness and other parameters from materials such as graphene, TiN, GaN, PEDOT, ITO, NbC, ALD, spin coated photo-resins. The maps provide information about the homogeneity and quality. Similar characterization is currently done by nano-scale methods, such as confocal Raman spectroscopy, Atomic Force Microscopy, or Transmission Electron Microscopy, and/or macro-scale methods [1], such as van der Pauw or optical microscopy. However, nano-scale methods are slow and cannot characterize large surfaces. Macro-scale methods generate characterization that average the magnitudes and, thus, cannot provide localized information.

Onyx provides meso-scale characterization and covers the gap between nano-scale and macro-scale methods. Onyx is a terahertz-based system [2] that works in reflection geometry as opposed to state-of-the-art methods [1-3] and provides conductance and resistance maps in the terahertz range.

Figure 1 shows the conductance maps of two 8" wafer. Sample A shows the conductance of a bare Si wafer while sample B shows the conductance of a 8" Si wafer cover with a 40nm TiN film deposited by ALD. As it is possible to see, Onyx provides information about the conductance of the sample and the quality of the ALD deposition process. This analysis where performed in less than 1 hour and a full map of the samples where obtained. The results are in excellent correlation with van-der Pauw method [4].

Onyx can be integrated with reactors and enable monitoring production in real-time. Therefore, Onyx could support the production of graphene at industrial scale. Onyx can implement characterization standardized protocols for accurate and repeatable measurements.

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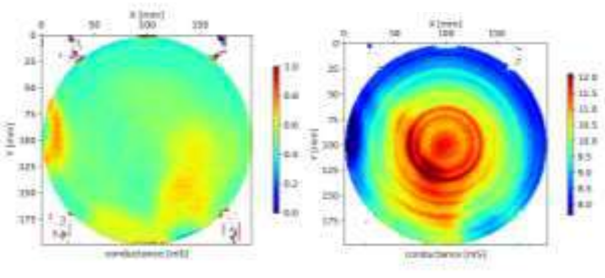

(a) (b)

Figure 1: Conductance maps of two samples: (a) 8" Si wafer and (b) 40 nm TiN film over Si substrate at 0.5 THz.

Graphene for quantum electrical metrology and the revised International System of units SI

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The quantum Hall effect and the Josephson effect have revolutionized the electrical measurements by providing universal and highly reproducible realizations of the units ohm and volt related to the elementary charge e and Planck's constant h, only. In 2018, these quantum electrical standards will culminate in the revision of the International System of units SI based on fixing several fundamental physical constants (Fig. a). The next challenges concern the extension of their applications, the simplification of their use for broadened dissemination towards industrial end-users and their integration in more complex systems. Graphene can play a critical role towards these objectives. At LNE, with graphene grown by CVD on SiC, we have recently demonstrated robust Hall resistance quantization with state-of-the-art accuracy ($<10^{-10}$) in relaxed experimental conditions (magnetic field down to 3.5 T (Fig. b), temperature up to 10 K or current up to 0.5 mA), much easier than those required by GaAs/AlGaAs devices [1]. These conditions are compatible with integration of the standard in a compact, simple-to-operate and lower-cost cryogen-free system. In addition, the reduction of the operation magnetic field (expected down to 1 T) renders possible the integration of the graphene-based quantum Hall resistance standard with metrology superconducting devices. This is a big advantage to miniaturize a recent experiment that we have performed at LNE. Actually, by the combination of a quantum Hall resistance standard, a Josephson voltage standard and a SQUID-based cryogenic transformer arranged in an original circuit, we have demonstrated a programmable quantum current standard related to e and realizing the ampere with unprecedented accuracy (10^{-8}) [2]. Beyond, we are currently assessing the integration on a graphene chip of various quantum electrical metrology devices. Based on graphene, we can now consider the perspective of a universal and highly accurate quantum electrical multimeter. Such a device will contribute to realize and disseminate the advantages of the revised SI and will considerably improve electrical measurements.

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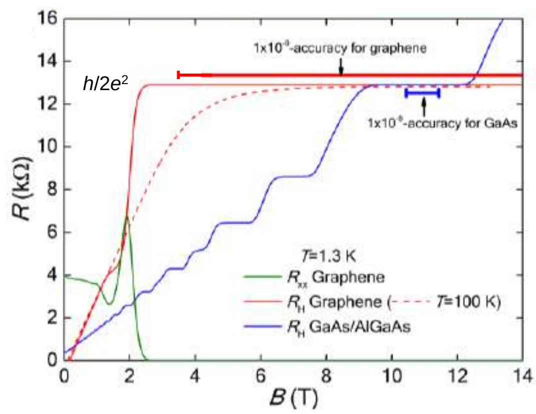
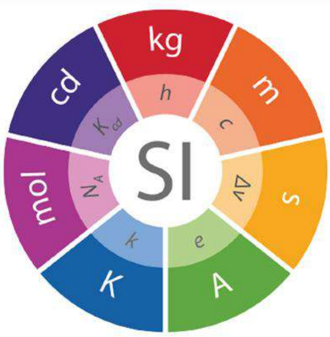


b)



a)

Figures : a) The revised SI based on fundamental constants. b) Hall resistance (R_H) and longitudinal resistivity (R_{xx}) as a function of the magnetic flux density in a Hall device based on CVD graphene on SiC (GaAs/AlGaAs device for comparison)

Defects in Metal Dichalcogenides: Effects in Catalysis & Optical Emission

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We will first focus on: *1)* defining the dimensionalities and atomic structures of defects [1[; *2)* pathways to generating structural defects during and after synthesis and, *3)* the effects of having defects on the physico-chemical properties and applications [2-4]. We will also emphasize doping and allowing monolayers of MoS_2 and WS_2, and their implications in electronic and thermal transport. We will also describe the catalytic effects of edges, vacancies and local strain observed in $Mo_xW_{(1-x)}S_2$ monolayers by correlating the hydrogen evolution reaction (HER) with aberration corrected scanning transmission electron microscopy (AC-HRSTEM). Our findings demonstrates that it is now possible to use chalcogenide layers for the fabrication of more effective catalytic substrates [3], however, defect control is required to tailor their performance. By studying photoluminescence spectra, atomic structure imaging, and band structure calculations, we also demonstrate that the most dominating synthetic defect—sulfur monovacancies in TMDs, is responsible for a new low temperature excitonic transition peak in photoluminescence 300 meV away from the neutral exciton emission. We further show that these neutral excitons bind to sulfur mono-vacancies at low temperature, and the recombination of bound excitons provides a unique spectroscopic signature of sulfur mono-vacancies. However, at room temperature, this unique spectroscopic signature completely disappears due to thermal dissociation of bound excitons [4].Finally, hetero-interfaces in TMDs, will be studied and discussed by AC-HRSTEM and optical emission.

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Figures

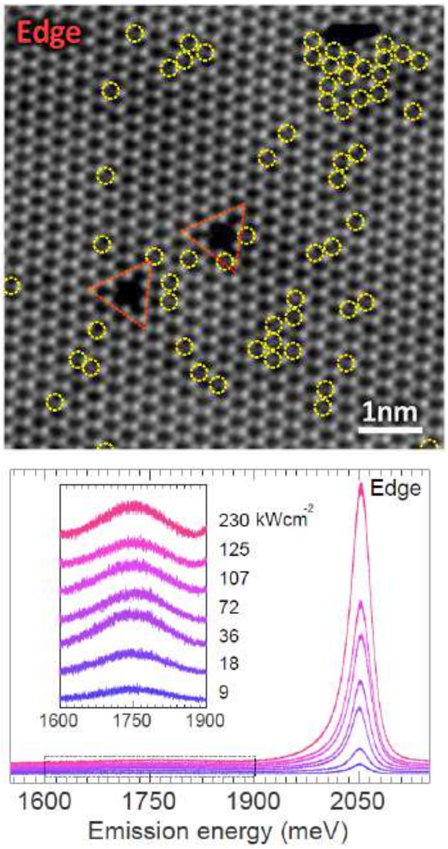

Figure 1: Top. AC-HRSTEM image of the edge of a WS_2 triangular monolayer showing more vacancies at the edges. Bottom. Evolution of the PL spectra at the edges of a triangular WS_2 monolayer with high concentrations of sulphur mono vacancies at the edges.

Using graphene as epitaxial substrate and transparent electrode for AlGaN UV LEDs

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We have recently developed a generic atomic model, which describes the epitaxial growth of semiconductor nanostructures on graphene that is applicable to all conventional semiconductor materials [1, 2]. Recently we have also shown the vertical growth of dislocation-free GaN nanowires on graphene mediated by nanometer-sized AlGaN nucleation islands [3]. The epitaxial growth of semiconductor nanostructures on graphene is very appealing for device applications since graphene can function not only as a replacement of the semiconductor substrate but in addition as a transparent and flexible electrode for e.g. solar cells and LEDs.

For deep UV AlGaN based LEDs, in huge need for various disinfection and sterilization purposes, the concept offers a real advantage over present thin film based technology. Such thin film UV LEDs are today very expensive and inefficient due to the lack of a good transparent electrode, the high dislocation density in the active thin film layers, low light extraction efficiency, and the use of very expensive semiconductor substrates (e.g. AlN). NTNU and CrayoNano are now developing UV LEDs based on AlGaN nanostructures on graphene, which potentially can overcome all these problems. A proof-of principle flip-chip UV LED, will be presented at the meeting.

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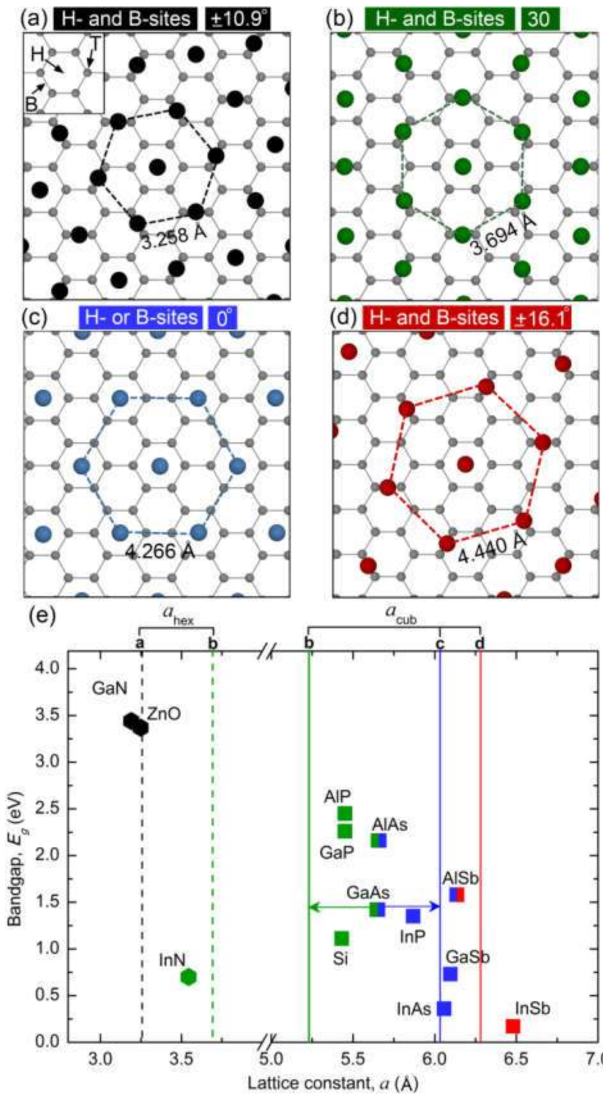

Figure 1: (a-d) Relative orientation and arrangement when semiconductor atoms are adsorbed on H- and/or B-sites. (e) Generic model describing the semiconductor bandgaps vs. lattice constants together with lattice constants for the lattice-matched atom arrangements on graphene [1].

Upcoming applications of graphene oxide and graphene oxide derivatives

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Abstract

Graphene oxide (GO) has the tremenduos advantage of being a material easy to modify to become compatible with a wide range of requirements. In its virgin state, it is a highly oxidized solid acid easily dispersible in polar solvents as single layers 1 nm thick. GO can be reduced to become more or less graphene-like rGO, and both GO and rGO can be de-acidified, nitrogen doped and functionalised to obtain new properties. GO and GO-derivatives (Fig. 1) have been reported to have potential for a range of applications, such as corrosion protection, water treatment, composites, lubricants, energy storage, photo-catalysts, sensors, sports equipment and medical. Abalonyx, as a specialised graphene oxide producer is continuously monitoring up-coming applications with the ambition to provide optimized GO-products for industrial applications.
From an industrial end-user perspective, concerns apart from relevant chemistry are costs, availability and hazards. Costs are strongly related to production volumes (Fig. 2) and availability is related to proven production capacity, preferably by more than one producer. Regarding hazards, the picture is not yet complete, especially related to interaction with cells, being the subject of several recent studies.
Building credibility in all aspects is a step by step process, that is now underway.

Figures

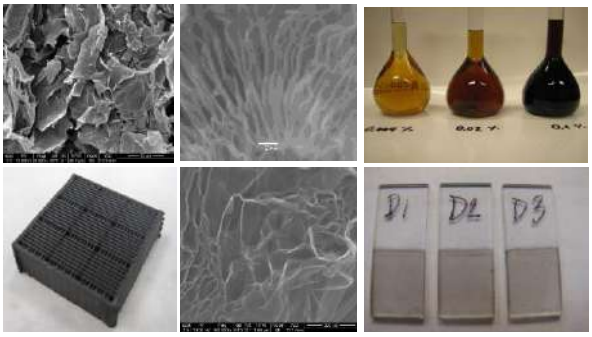

Figure 1: Examples of GO and rGO in different forms: powders, disperions, scaffolds, aerogels and transparent conductive films.

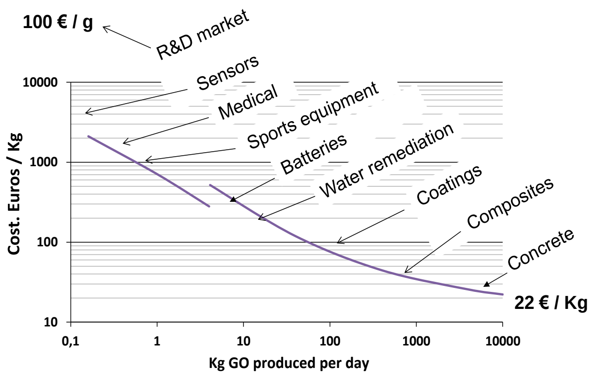

Figure 2: Cost predictions for GO as a function of volumes produced per day, with indicated cost tolerances for selected potential markets and applications

Towards graphene applications in electronics

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Abstract

Since the discovery of graphene many promising applications have been identified. Furthermore, graphene has shown to have a great potential to be applied in electronics, optoelectronics and photonics. Many multifunctional working prototypes have been demonstrated using CVD (Chemical Vapour Deposition) graphene. The successful introduction of graphene into the semiconductor industry will require the development of Complementary Metal-Oxide Semiconductor (CMOS) compatible CVD graphene [1]. Depending on the type of application and the function of the graphene in the device, the integration scenario could vary from front to back-end. However, all the integration scenarios will require a scalable, uniform and high-quality graphene. Therefore, uniformity, high charge carrier mobility and controlled doping at wafer scale are the current focus from the material production perspective. In addition, there are many other factors that have to be taken into consideration during the fabrication of graphene devices at wafer scale [2] including contact resistance [3], encapsulation [4,5], type of substrate, uniformity, etc. During this talk I will cover challenges related to the graphene production and device fabrication at wafer scale.

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GRAPHIN2018 – ORALS

Lab-on-a-chip DNA sensor based on graphene electrolyte-gated field-effect transistors

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Lab-on-a-chip (LoC) for the detection of complex diseases are growing in importance and normally require the detection of multiple targets in an autonomous and portable fashion. Taking advantage of graphene low-dimensionality, high carrier mobility and chemical stability, we developed a monoplex assay based on DNA label-free sensors, made of graphene electrolyte-gated field-effect transistors (FETs) in a relatively simple design, with high sensitivity and transducing capability. Graphene geno-FETs with a receded, integrated gate architecture [1], are fabricated at the 200 mm wafer scale, for detection of synthetic DNA sequences. The graphene FETs were manufactured by patterning gold contacts on an oxidized silicon substrate [2], passivating the current lines and transferring CVD-grown graphene. To ease practical experiments, we developed a reading platform, composed of a disposable graphene FET chip, optionally wire-bonded to an inexpensive chip carrier, and a credit card format electronic control board including: a 16 bit digital-to-analogue signal generator, generating the gate voltage sweep, a current source component, a 16 bit analogue-to-digital converter, and a CMOS matrix switch array to address up to 24 contacts, used to address a common gate, a common source, and up to 22 individual sensor drains. The board is controlled by a 32 bit microcontroller and communicates with a host computer by a USB, which also powers the board. A laptop computer, with a custom software, is used to control the experiment.

The LoC measures transfer curves of the transistors as a function of time and tracks the gate voltage corresponding to the maximum channel resistance. This voltage is, in turn, dependent on the modulation of the electric double layer that forms at the interface between graphene and the droplet containing the target DNA, whenever hybridization between probe and target DNA occurs. The graphene device is able to detect the target DNA in concentrations down to 10 aM, in a range up to 10 fM.

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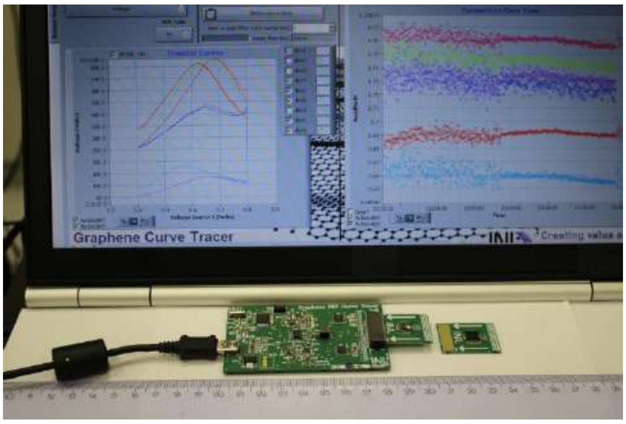

Figure 1: Picture of the measurement system.

PolyGraphene - Perspective Enterosorbent for Medical Toxicology. Preclinical Tests and Safety Assessment.

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The main task. To investigate the interaction of carbon sorbent of new-generation PolyGraphene with the structure of the small intestine mucosa and to determine the possibility of using PolyGraphene for detoxification. During experiments it was studied a new form of an expanded graphite, which after repeated thermal activation and chemical modification with using ultrasound results in a material with stacks of carbon layers with higher multiplicity (10-100), but containing both single sheets of graphene. It is possible to include this material in classification of nanocomposite sorbents and the graphene-containing carbon forms. The authors of this work introduce a new classification of this type of material and see it as PolyGraphene (PG).
Enterosorption - the method based on linkng and removal from the digestive tract (DT) with the medical or preventive purpose of endogenous or exogenous substances, metabolites, various products of a microbic origin.
The last achievements in the field of physiology and pathology of digestion allow to consider enterosorption mechanisms from mass exchange positions between the internal and enteral medium. Though materials and manufacturing techniques of sorbents significantly differ, the main medical requirements to enterosorbents remain rather constant: 1) convenient pharmaceutical form; 2) not toxicity; 3) preparations shouldn't injure the mucous; 4) there has to be a good evacuation warning a sorbent congestion in an intestines gleam; 5) high sorption ability to the deleted components; and others.
Conditions of experiments. Histologic research of a small intestine. For 10 rats through a probe was entered PoliGraphen's suspension into initial department of a duodenum. After 2.5 hours for receiving samples of biomaterial to rats was done euthanasia according to the European bio-ethical standards of manipulations with laboratory animals. Further was opened an abdominal cavity of rats, was cuted sites of medial department of a duodenum, initial department of lean gut and distal department of ileum gut. Samples placed in the cooled fixating solution and processed according to the standard scheme for histologic research.
The results. PolyGraphene remains as a part of a himus and in the field of near wall of a mucous membrane of a gut. PG doesn't get directly to a surface of cages of an epithelium that treats as large poly-particles of PG (100-500 microns), and smaller poly-particles (10-50 microns). At one-time introduction of PG, it goes as transit goods through a small intestine, without being late and without getting directly to a surface of an intestinal epithelium which is closed by a continuous dense mucous bed, and also in space between intestinal fibers. PG works, mainly in a gleam of intestines and at a surface of a mucous layer, without having direct negative destructive effect on cells of an intestinal epithelium and PG has a large capacity.
Conclusions. The results of tests PG as acting basis for the enterosorbents of new generation indicate a good promising potential for wide medical applications of PolyGraphene.

Biosensing and imaging with graphene based platforms

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Ultra-sensitive detection and diagnosis are of vital relevance for biomedical applications. We are thus developing two kinds of sensors based on graphene for the detection, quantification and imaging of molecules and biomarkers.

The first one is based on the covalent functionalization of graphene by adding carboxyl acid groups which allow successive binding with different biologically active molecules for antigen sensing applications. Up today, graphene oxide derived materials are used for these applications, however, the presence of high fractions of other functional groups, low conductivity and reproducibility problems are important limiting issues. We present a new approach for specific surface functionalization of graphene: during the CVD growth, highly conductive COOH functionalized monolayer or few-layer graphene is generated. The homogeneity and functionalization degree are evaluated combining micro-Raman and XPS spectroscopies. The COOH content is around 5 %, which corresponds to an average inter-spacing < 1nm, adequate to accommodate antibodies. Moreover, the relative concentrations of the other functional groups are lower than for graphene oxide derived materials. The obtained electronic transport characteristics (sheet resistance ~7 kΩ and mobility ~800 cm^2/Vs) are very adequate for sensing using the change in conductivity induced by antigen anchoring. The bio-molecules detection is carried out through the immobilization of antibodies (IgG1– with a green fluorophore) by the carbodiimide method, which allows the formation of a strong amide bond. The anchoring is demonstrated to be effective by comparing bare and functionalized graphene fluorescence images.

The second kind focuses on enhancing the analyte Raman signal. Raman spectroscopy is a non destructive easy to use specific technique but with low sensitivity. Here we present how interference enhanced Raman scattering (IERS)[1] in adequately designed ordered porous alumina structures provide interesting amplification factors We have designed and fabricated, according to the calculations, Al_2O_3 membranes from Al where the Al_2O_3 layer at the pore base has been reduced down to < 5nm. Transferred graphene on top of these membranes is used here to reveal the amplification power of the tested platform and as the appropriate substrate for the deposition of organic molecules. The overall IERS amplification is > 400 and, optimized membranes for IERS combined with metallic nanoparticles can lead to IERS + SERS combined effects with excellent amplification values.

Figures

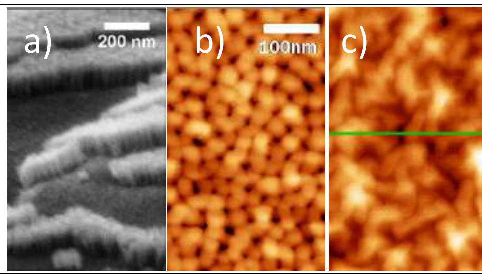

Fig. 1: Alumina porous membrane: SEM (a) and AFM (b) images; c) AFM image with graphene

1 L. Alvarez-Fraga, E. Climent-Pascual, M. Aguilar-Pujol, R. Ramirez, F. Jiménez-Villacorta, C. Prieto, A. de Andrés ACS Appl. Mat. & Interfaces 9, 4119 (2017)

Asymmetric dual grating gate graphene FETs for direct detection of Terahertz radiation

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The unique optical and electronic properties of graphene open the way for the development of new graphene-based devices for terahertz technology. Exfoliated graphene shows a high value of electronic mobility at room temperature [1] and even higher at low temperatures. Applications of graphene field effect transistors (GFET) operating in the terahertz (THz) range are appealing as it is one of the least explored frequency regions and holds potential to revolutionize different fields like security, medical imaging or high-speed wireless communication. Recent research on vertically stacked heterostructures of graphene with hexagonal-boron nitride (h-BN) and other two-dimensional materials has opened a new realm for intriguing device physics making them ideal candidates for future high-frequency technology [2–3].
We report on direct detection of terahertz radiation by using graphene-based FETs with asymmetric grating gates (ADGG GFETs). The device was fabricated with a stack of h-BN/Graphene/h-BN on SiO_2/Doped-Si. The former layer was used as a back gate as well as an asymmetric dual grating top gates (Fig.1). It was subjected to terahertz radiation at frequencies of 150 and 300 GHz from 4K up to 300 K and a clear photocurrent was observed (Fig.2).

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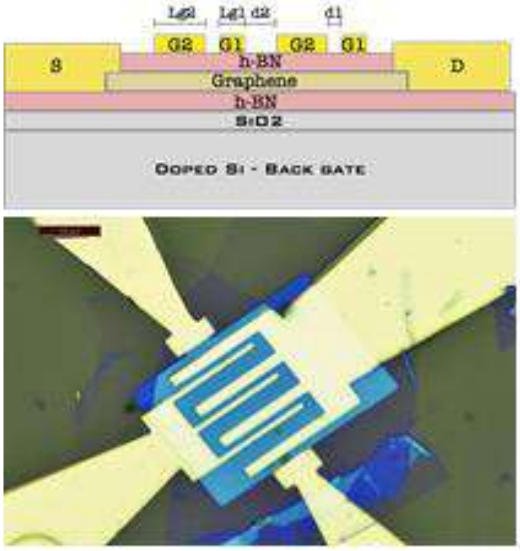

Figure 1: Side description of the GFET structure and top view microscopic image of the GFET

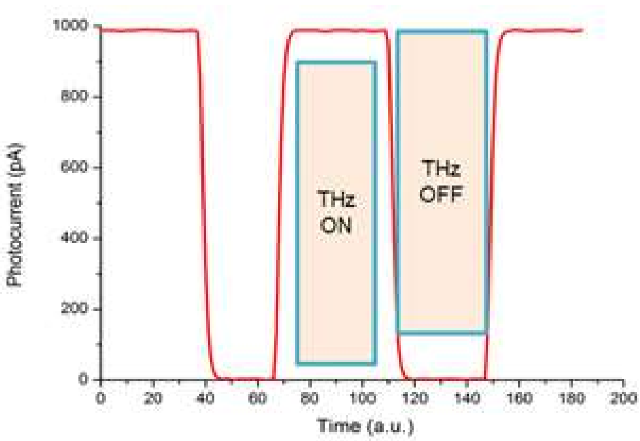

Figure 2: Photocurrent vs time when the THz beam at 300 GHz was switched on and off.

Transcriptomic and single cell interaction properties of graphene in human primary immune cells.

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Abstract

Despite significant progress of nanotechnology also in medicine, the development of new nanomaterials able to treat and prevents diseases such as cancer is still one of the biggest challenges [1]. In this challenge, a critical step is represented by the assessment of their impact on the complexity of the immune system [2]. Graphene oxide (GO), has attracted tremendous interest being explored for many potential applications in medicine [3]. To clarify its action on the immune cells, here, we propose an integrative analytical pipeline encompassing genomic and cellular characterization of the impact of graphene on primary immune cells. We used whole-transcriptomic analysis (Illumina BeadArray) for functional and molecular characterization of GO and GO functionalizated through the addition of amino groups ($GONH_2$) on human T-cells and monocytes. We then employed single cell mass cytometry. We identify 15 cellular main populations corresponding to 200 nodes of distinct but logically interconnected cell sub-populations. Notably, thanks to several analytical tools (i.e.SPADE and viSNE) we found that only the functionalized $GONH_2$ was able to induce a specific dendritic cell and monocyte activation skewed toward a Th1/M1 response, as demonstrated by the increased production of classic M1 cytokines (TNFa, IL6, and CCL4) [Figure 1]. This effect was proved also by the overexpression of pathways critical for the development of an effective anti-tumor immune response (i.e. interferon signalling, CCR5 and CXCR3 ligands) [Figure 2]. Our findings report a new pipeline able to carefully analyse the immunological impact of new nanoscale platforms for a successful application in medicine.

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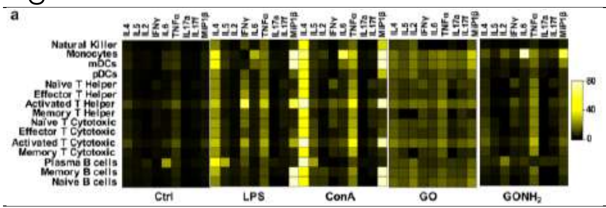

Figure 1: Heat map analysis of the immune cell behavior using CyTOF.

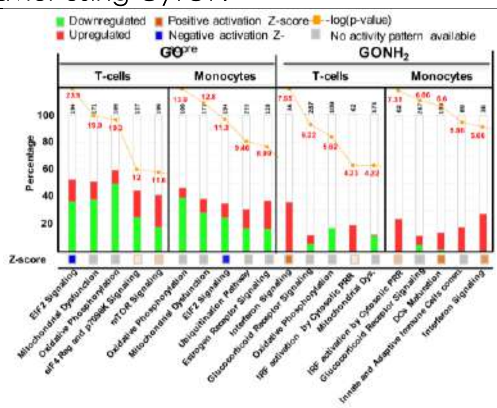

Figure 2: Gene expression impact of GO and $GONH_2$ on T- and monocyte cell lines.

Production of Nitrogen Doped Graphene Oxide

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Abalonyx, established in 2005, has worked extensively with synthesis and characterization of graphene oxide (GO) and reduced graphene oxide (rGO). Specifically, GO is produced according to a proprietary modified Hummer method from different raw materials, subjected to size fractionation and further surface chemical modification by ultrasound, heat treatment, washing, dialysis and addition of surface active reagents. Abalonyx has also successfully scaled up its production capacity for rGO from lab-scale of about 25 g/day to 0.5 Kg/day. This has been achieved by arranging continuous feeding of GO-powder into an oven with an automated powder dozer.

Abalonyx has started production of new series of functionalized/ doped products for specific applications. As an example, nitrogen doped graphene derivatives have received attention recently due to their use in electrolyte membrane fuel cell applications. It is worth mentioning that introduction of N to GO/rGO results in three primary N- bonding configurations including the pyridinic N, pyrrolic N, graphitic N and N-oxides. Both quaternary N and pyridinic N moieties have been suggested to facilitate oxygen reduction reaction (ORR).

Abalonyx is a partner of an EU project entitled **"NanoElMem"**and our main task is production of NGO/NrGO. For this purpose two different approaches were selected. In the first one, a simple, rapid and scalable wet-chemical method was selected for the synthesis of NGO only by ultrasonic treatment of GO in aqueous solution of ammonia and in the second approach, GO was placed in a chamber and exposed to NH3 gas in a "cold" plasma generator. The experiment was done at room temperature. A comprehensive characterization study was done (The FTIR and XPS spectra for our GO and NGO has been shown in Figure 1 and 2 as examples). This work compares the results obtained for Synthesis of NGO by ultrasonic and plasma treatment.

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www.abalonyx.no
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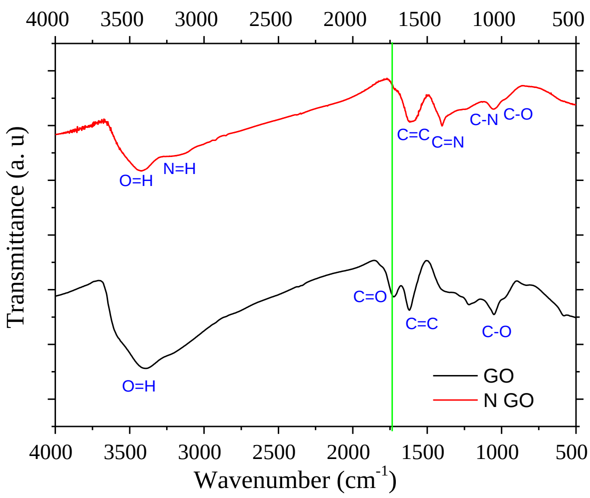

Figure 1: *FTIR spectra of GO and NGO.*

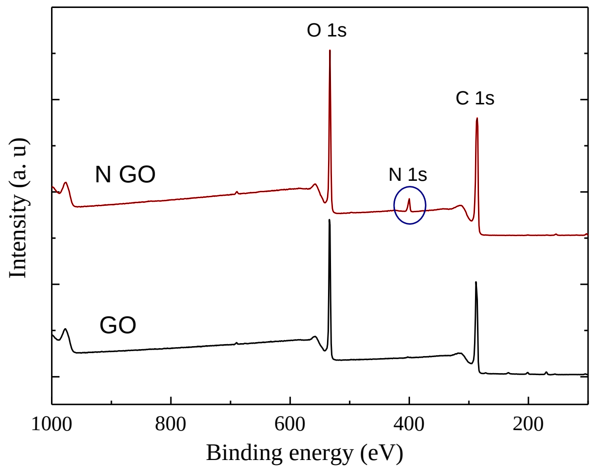

Figure 2. *Wide-survey XPS spectra of GO and NGO samples.*

pH Measurement with Large-Area Graphene Field-Effect Transistors at the Quantum Capacitance Limit

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Graphene field-effect transistors are attractive candidates for sensing applications [1] because of their high charge carrier mobility and a relatively inexpensive fabrication process for large area devices [2]. However, it remains a challenge to integrate high quality analyte selective layers on graphene without compromising mobility or capacitive coupling [3]. We demonstrate here graphene-based ion-sensing field-effect transistors that saturate the physical limit of sensitivity. We present a model outlining the necessity for maximizing the device carrier mobility, active sensing area, and capacitive coupling in order to minimize noise. We encapsulate large-area graphene with an ultrathin layer of parylene, a hydrophobic polymer, and deposit an ultrathin, stoichiometric pH-sensing layer of either aluminum oxide or tantalum pentoxide. With these structures, we achieve gate capacitances ~ 0.6 μF/cm2, approaching the quantum-capacitance limit inherent to graphene, along with a near-Nernstian pH response of ~55±2 mV/pH. We observe field-effect mobilities as high as 7000 $cm^2V^{-1}s^{-1}$ with minimal hysteresis as a result of the parylene encapsulation. A detection limit of 0.1 mpH in a 60-Hz electrical bandwidth is observed in optimized graphene transistors [4].

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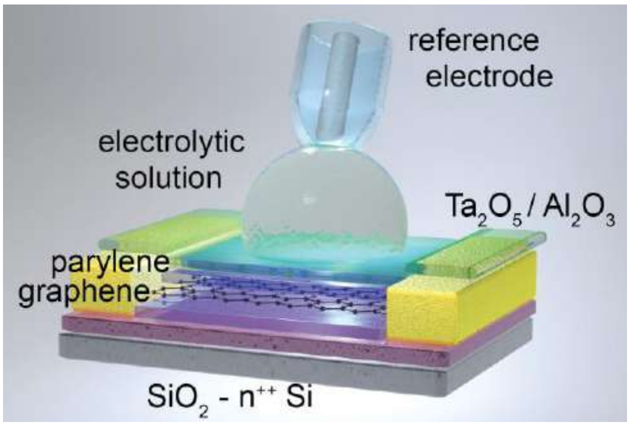

Figure 1: Schematic of graphene ISFET encapsulated with parylene and a layer of metal oxide (Ta_2O_5 or Al_2O_3) on a Si-SiO_2 substrate.

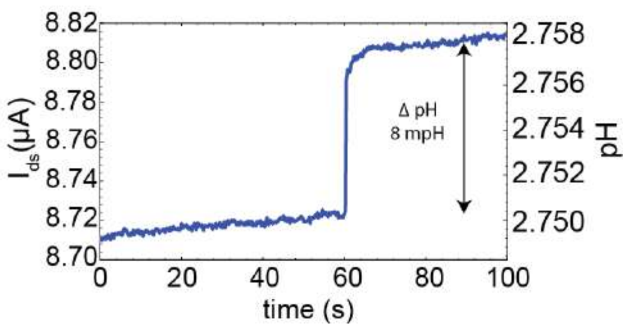

Figure 2: The change in current Ids of an ISFET with time after increasing the pH by 8 mpH at t=60 s, resulting in 85 nA of change in current.

Dirac Fermion Reflector as a Scattering Length Meter

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Electron propagation in ballistic graphene bears strong analogies with optics, with the Fermi energy as the optical index and p-n junctions acting as dioptres [1,2]. Using nano-patterned bottom gates (Fig. 1) and h-BN encapsulated graphene, we create a prism-shaped doping profile acting as a Dirac fermion (DF) reflector.

We demonstrate the reflection effect and the full tunability of the DF optical index in agreement with a scattering model (Fig. 1). The DF-reflector operates at large negative gate voltage (V_{g1}) where the DFR resistance saturates according to the finite scattering length.

The DFR device is a sensitive meter of scattering length in the range 0.6-6 µm. It is used in Fig. 2 to measure the phonon scattering length in good agreement with theory.

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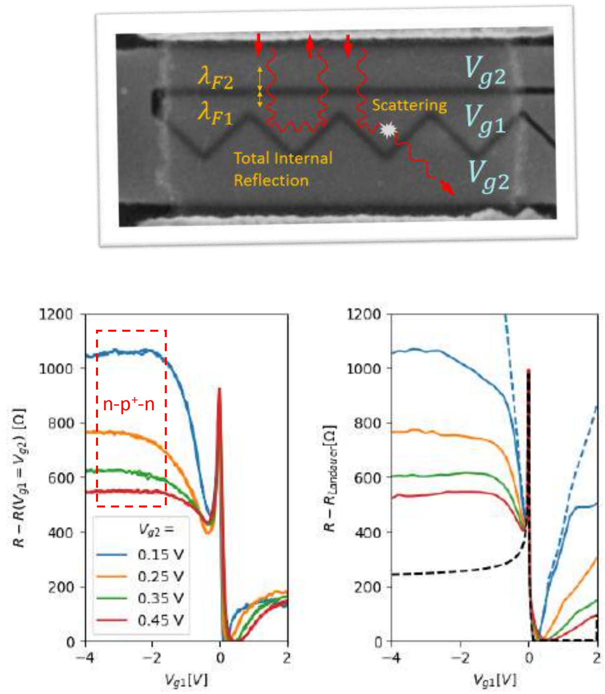

Figure 1: *Top*: Illustration of the Dirac Fermion Reflector. *Left*: Device resistance as a function of V_{g1} for various V_{g2}. The red box indicates the operation regime of the reflector. *Right*: Simulation taking into account scattering lengths ranging from 0.7 to 2.8 µm. We also show the case of no scattering and of a rectangular gate (blue and black dashed lines, respectively).

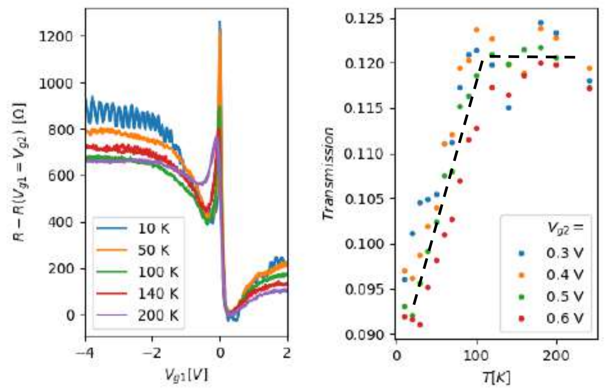

Figure 3: *Left*: Characterising the Dirac Fermion Reflector at various temperatures (V_{g2}=0.3 V). At low temperatures, resistance oscillates as a signature of coherent DF optics. As we increase the temperature, we see the plateau resistance decrease, i.e. the residual transmission (*right*) increases steeply.

Graphene as substrate for selective self-assembly of 2-D materials for optoelectronic applications

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Graphene is well known as archetype of the 2-D materials, it is a multifaceted species widely recognized for a broad range of applications, including (opto)-electronics due to its outstanding ambipolar charge carrier mobilities and high transparency. These factors together with the highly ordered 2-D structure, makes graphene an ideal substrate for the growth of layered structures, enabling the assembly of heterostructures with graphene as the key step for the realization of complex hybrid device architectures. In optoelectronic applications, a proper electrical contact is critical for the optimal functioning of the device and graphene has been identified as a very efficient ambipolar charge carrier thus it is possible to use it as electrode. Recently, we achieved highly selective growth of PEDOT on patterned graphene, providing unique hole-conducting/electron-blocking heterostructures. This achievement tempted us to investigate the formation of other graphene heterostructures in a selective fashion and to explore their potential for (opto)-electronic applications. Here, we describe a highly efficient process of selective and oriented growth of various 2-D crystalline materials (optically active) on monolayer graphene. To achieve this we have chosen different organic precursors for the active material which is composed of alternated organic and inorganic layers. Varying the length of the aliphatic chain or size of the aromatic moiety (present in the organic part) affects the selectivity of film formation on graphene due to the hydrophobic interactions and/or π–π stacking, respectively. Thank to this, high spatial resolution down to 5 µm was achieved, as well as uniform coverage of up to centimeter scale graphene sheets.

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Binding energies of exciton complexes in two-dimensional transition metal dichalcogenide

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Abstract

Excitonic effects play an important role on the optoelectronic behavior of atomically thin two-dimensional crystals of the tungsten transition metal dichalcogenide (TMD). Neutral and charged exciton behaviors in monolayer (ML) TMD are handled within effective-mass approximation in which the critical parameters are ensured from our ab-initio calculations. Firstly, we reveal an exciton series with a novel energy dependence on the orbital angular momentum. We show that, states corresponding to higher angular momentum have a larger binding energy than those corresponding to lower angular momentum. We either demonstrate that the trion with two heavier identical carriers has a larger binding energy [1]. Considerable control of the dielectric environment on exciton binding energy is elucidated in Fig.1. Secondly, we use the equilibrium mass action law, to quantify the relative weight of exciton and trion PL. We show that exciton and trion emission can be tuned and controlled by external parameters like temperature, pumping and injection electrons [2]. Thirdly, localization of neutral exciton center of mass motion arising from ML defect has been also studied (Fig.2). Our obtained results are in agreement with available experimental works [3].

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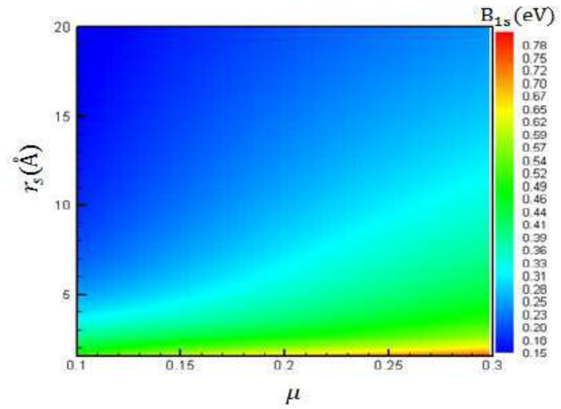

Figure 1: Color surface plot of the exciton binding energy B_{1s} in ML WS_2. Calculations are performed over a range of material screening lengths rs and possible exciton reduced masses μ. The average dielectric constant of the surrounding material is $\kappa = 2.5$.

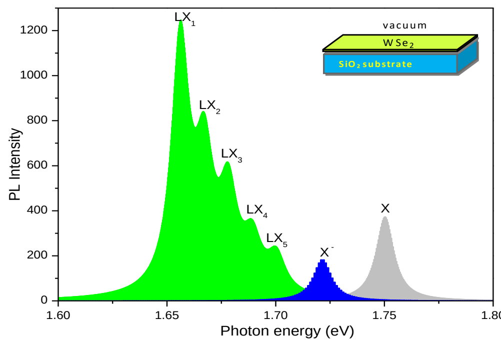

Figure 2: One-photon PL spectrum for free, localized exciton and trion in ML WSe_2 at a temperature of T=10 K. The spectrum shows five pronounced PL peaks, which are located between 1.62-1.72 eV. The emission from the neutral and charged exciton is substantially reduced in the presence of localized states.

Controlling the size, number of layers and planarity of CVD graphene single-crystals

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Chemical vapor deposition (CVD) of graphene on copper catalyst is presently considered as the most promising manufacturing approach as it yields large-area graphene with a relatively good control over the structural quality and the number of layers. In order to benefit from graphene's excellent physical properties and fully exploit its potential in advanced technological applications, it is essential to precisely control the CVD process.

Our work focuses on studying the correlation between the conditions employed during the CVD protocol, the type of Cu substrate and the graphene growth results. The last findings which have been made recently in order to reduce the presence of structural defects, limit the thickness to one single layer and prevent the formation of wrinkles and cracks will be presented.

CVD protocols typically consist of four successive steps: the CVD furnace warming, the high temperature Cu annealing, the graphene growth, and the furnace cooling. First, we systematically studied how graphene growth conditions (CH_4 partial pressure, H_2-to-CH_4 ratio, pressure) influence the density, the shape, the structural quality and thickness of graphene domains [1]. We then investigated how the conditions (gas composition, pressure) employed during the furnace warming and Cu annealing steps impact graphene nuclei density and number of layers [2]. Among other results, we found that two different kinds of graphene multilayer growth mode can take place: compact ad-layers formed via the diffusion of carbon species through the Cu foil bulk and branch-like multilayer regions formed through the diffusion of C species on the Cu surface (see Fig. 1) [2]. Finally, we found that employing a thin Cu film pre-deposited on a flat and rigid substrate (fused quartz or crystalline sapphire) as catalyst instead of commonly used Cu foils is essential to improve graphene's planarity and physical integrity (see Fig. 2).

Our findings provide clear guidelines to produce ultra-flat defect-free single crystals of graphene with a lateral size exceeding a few millimetres and a controllable number of layers.

Figures

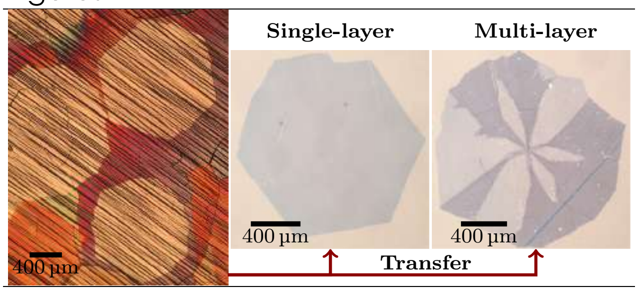

Figure 1: Millimeter-size graphene domains grown on Cu foils. Left panel: On Cu after a slight oxidation to make graphene visible. Right panel: transferred single-layer and branch-like multilayer domains (from [2]).

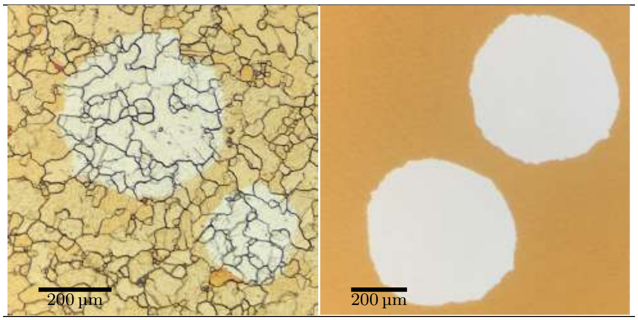

Figure 2: Graphene domains grown on (left panel) polycrystalline and (right panel) single-crystalline Cu films after a slight Cu oxidation to make graphene visible.

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Unravelling the boron nitride flakes morphology to enhance polycarbonate performances

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Abstract

The outstanding improvements of two-dimensional (2D) crystals-based composites in mechanical, electrical and thermal properties compared to pristine polymer matrices [1,2], have boosted the research activity in both 2D-crystals and polymer science fields.

A key requirement for the application of 2D-crystals in the composites field relies on their large-scale production [1,2]. In this view, liquid phase exfoliation of layered-crystals is one of the most promising approaches for the scalable production of high-quality 2D-crystals [3,4]. However, the dependence of the 2D crystal flakes morphology, *i.e.*, lateral size and thickness, on the mechanical properties of the polymer composites is not fully undestood yet.

Herein, we tackle this issue by designing an environmentally friendly approach, based on the exfoliation of bulk hexagonal-Boron Nitride (*h*-BN) in a water/surfactant solution [5] with controlled lateral size and thickness by using cascade ultra-centrifugation (Figure 1a) [6]. Our approach allows us to obtain two populations of flakes, named *h*-BN-s and *h*-BN-p samples, with aspect ratio, *i.e.*, lateral size over thickness, equal to 250 and 350, respectively. The *h*-BN flakes with tuned aspect ratio are subsequently used as filler in a polycarbonate (PC) matrix by exploiting solution blending, obtaining composite dispersions. The composites produced by using the fillers with higher aspect ratio have shown the highest mechanical performances, both in terms of stiffness and strength. The first is evaluated measuring the Young's Modulus, *e.g.* +22 % compared to the pristine PC matrix obtained at 0.1 wt% of loading of *h*-BN-s flakes *vs.* + 17 % obtained at the same loading of *h*-BN-p flakes (Figure 1b). The strength is instead evaluated measuring ultimate tensile strength, *e.g.* +12 % compared to the pristine PC matrix obtained at 0.1 wt% of loading of *h*-BN-s flakes *vs.* + 6 % obtained at the same loading of *h*-BN-p flakes.

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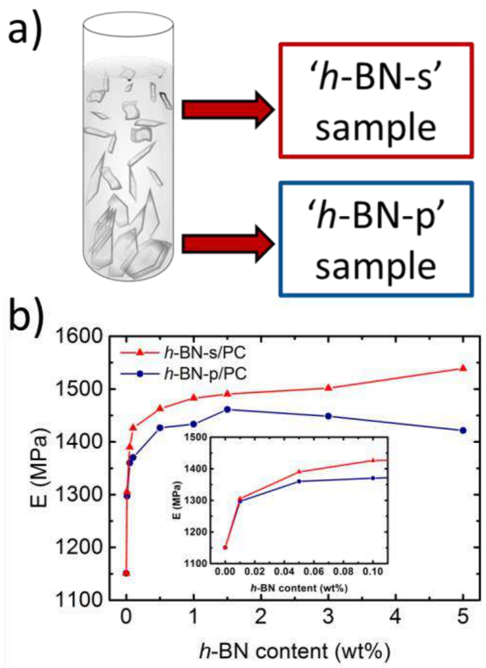

Figure 1: a) scheme of size selection of h-BN flakes by ultra-centrifugation; b) mechanical properties, expressed in terms of Young's Modulus, of hBN-s/PC (red), hBN/PC (blue) and graphene/PC (black) composites.

Functionalized and Oxidized Silicon Nanosheets for Sensors and Optoelectronics

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Until now, the number of transistors in a semiconductor circuit follows quite well Moore*s law. However, the scaling of silicon devices, on which the growth of semiconductor industry is currently based on, reaches its limits. Thus, research needs to find alternative solutions.

2D materials and with them also the monolayered silicon nanosheets (SiNSs) have much to offer. Novel physical properties, such as band gap and conductivity control can be very useful for device fabrication.[1] Nevertheless, ambient conditions, such as oxygen and UV light can easily destroy the SiNSs and convert it into silicon (di)oxide.[2], [3] Surface protection is therefore one of the crucial steps in 2D silicon treatment, before it can be applied in nanotechnology. Different covalent hydrosilylation reactions, either thermal, or initiated with various radical initiators, can be carried out with a variety of functional molecules. This modification step offers stabilization of the sheets for subsequent use. As a result, hybrid systems based on covalently bound molecules on SiNSs were synthesized, offering both materials' properties, which are present in the system.[5]

First, the hereby described hybrid materials were used for the fabrication of solution-gated field-effect transistors, which performance and physical properties are controllable *via* SiNSs' surface groups.[6] Additionally, a highly sensitive photonic sensor was built, showing light absorption starting with wavelengths lower than 450 nm.[7] Finally, the fabrication of a capacitive humidity sensor was performed, which sensitivity can also be easily tuned *via* surface molecules.

In summary, an introduction into a wide range of opportunities will be presented, which come with the ability of surface engineering of 2D silicon and the combination of different disciplines, such as Chemistry, Physics, Electrical Engineering and Nanotechnology.

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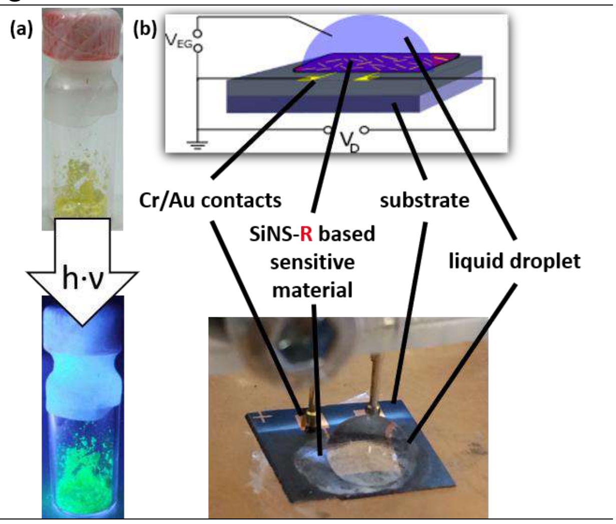

Figure 1: (a) Images of Silicon Nanosheets (SiNSs) under visible light (top) and UV radiation (bottom). The SiNSs emit green photoluminescence at λ = 510 nm. (b) Solution-gated field-effect transistor (SGFET) based on modified SiNSs, which were functionalized *via* hydrosilylation reaction. Properties of the SiNSs can be adjusted for the required application with the covalent modification of the surface.

Quality Assessment of 2D Materials: continuity, uniformity and accuracy of mobility measurements

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As the availability of large area graphene and other 2D materials increases, the ability to accurately assess uniformity and quality has become critically important. Assessment of the spatial variability in carrier density and carrier mobility (μ) can be difficult and time consuming, but variations must be identified and minimized. We present a simple framework for assessing the homogeneity of devices based on 2D-materials. The field effect in large-scale graphene CVD devices [1] (Fig. 1a) and devices of exfoliated graphene encapsulated in hexagonal boron nitride [2] (Fig. 1c) were measured in dual configurations (Fig. 1b inset). A gate-dependent effective homogeneity factor, *ß* is then derived (see Fig. 1b/d). Finite element simulations were carried out and suggest that inhomogeneity in spatial doping (as low as 10^{10} cm^{-2}) rather than inhomogeneity in μ is the significant cause of variations in inhomogeneity in the case of graphene. Such doping variations lead to systematic errors when calculating μ, which are hidden if the inhomogeneity factor is ignored. In addition, we find that for certain devices Raman mapping (Fig. 2a) can be used as input for finite element simulations and reasonable agreement is found between simulated and experimental gate-dependent data (Fig. 2b). We also present data which illustrates the usefulness of the inhomogeneity factor in semiconducting 2D materials *e.g.* MoS_2 [3] and ReS_2[4]. A recent comprehensive study can be found here [5].

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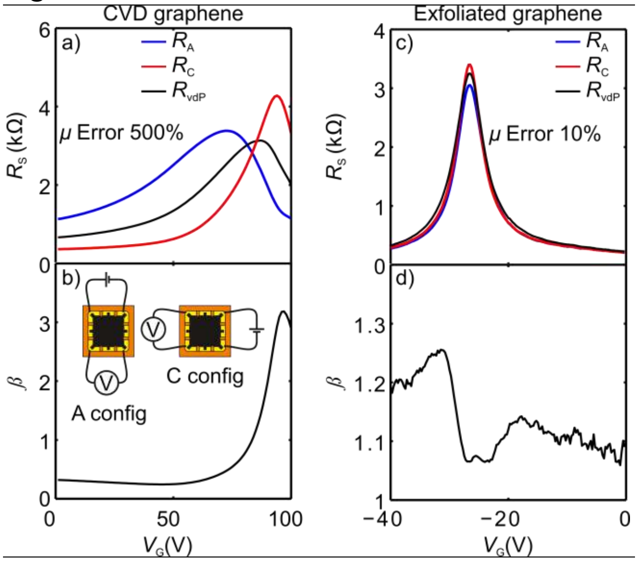

Figure 1:) CVD graphene device characteristics measured in the A config R_A, C config R_C, and calculated van der Pauw config R_{vdP}. b) Gate dependent device shape $ß = R_A/R_C$ for data from Fig 1.a. Inset: Configs A and C. c/d) Measurements for exfoliated graphene encapsulated in hexagonal boron nitride.

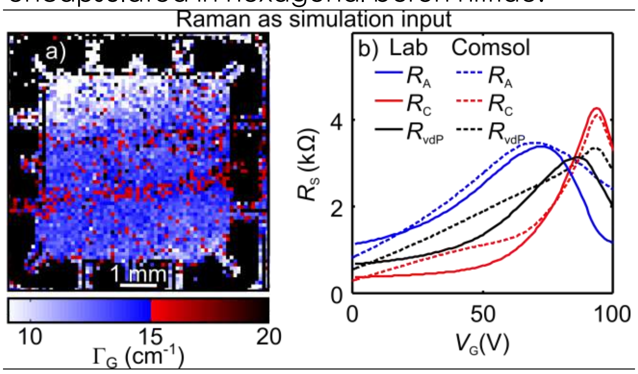

Figure 2: a) Raman map of 5625 spectra showing the FWHM of the G-peak (Γ_G). b) Comparison of electrical measurements (solid lines) and simulated gate data (dashed lines) using Raman maps as locations for isolating defects and doping.

Simulation and experimental investigation of 2D materials with far and near-field THz spectroscopy

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We show a direct comparison of the near and far-field THz spectroscopy used for characterisation of 2D materials. We demonstrate that the spatial resolution is dependent on the field detected (i.e. far or near-field), the limitation that arises from the detection scheme and the behaviour of the 2D materials when a THz field is applied. The observed material behaviour is also supported via simulations with Computer Simulation Technology (CST) software.

Fig. 1 shows the experimental results of the CVD graphene characterized with the far and near-field THz detection. The black squared area in the Fig.1a measured with our far-field setup (Picometrix© T-ray™ 4000) system is shown with a higher resolution in Fig.1c measured with the near-field spectroscopy via a low temperature Gallium-Arsenide photoconductive field detector [1]. As it can be observed the near-field detection will increase the spatial resolution, thus offering a more detailed characterization of the graphene quality.

The simulated structure shown in Fig.2a is a square shaped 1 layer graphene with side lengths of 40µm and another layer (shown in red) on top with side length of 20µm. The probes shown in Fig.2b are placed every 5µm throughout the sample and 51 layers of them every 10µm until 501µm mimic the cantilever structure used for the detection in the near-field setup. The thickness of one layer graphene and the high resistivity silicon substrate are 0.35nm and 525µm respectively. The excitation signal is a plane wave shown in Fig.2a and the simulation was done with 50.294.400 mesh cells.
Fig.3 shows the real part of the conductivity for the simulated graphene, where (a) is the theoretical calculated value via the Kubo formalism [2,3] (b) shows the detected value only with a single probe 11µm away from the sample and (c) as an average of all the probes, thus mimicking the cantilever. As it can be observed the path that the signal has to travel will distort the value of the conductivity, affecting of course also the spatial resolution that can be achieved with this method.

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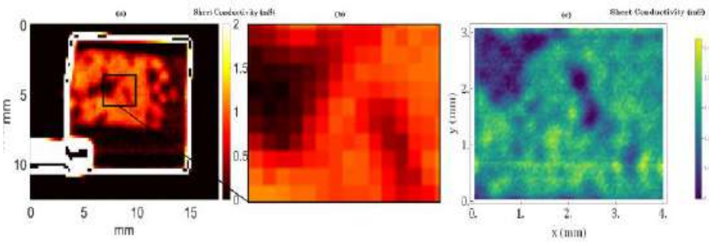

Figure 1: (a): Far-field sheet conductivity map of the CVD graphene, (b): Zoomed area of the indicated square in the first image, (c): Near-field sheet conductivity map of the area in (b)

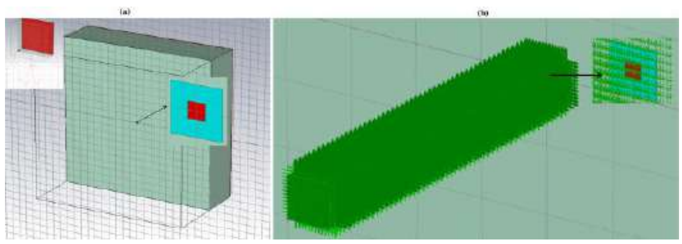

Figure 2: The simulated structure via CST

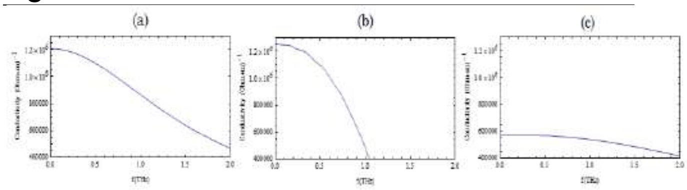

Figure 3: Real part of conductivity: (a) calculated with Kubo formalism, (b) from the probe 11µm away from the graphene sample, (c) average from all the 51 probes

Mathematical Calculation of Screened Coulomb Interaction Potential in Graphene.

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The wide interest in graphene and other 2D systems is due to their huge application potential. In turn, this is due to their unique physical properties. In addition, the presence of excitons and impurity centres (Coulomb pair) can significantly affect physical properties of grapheme [1]. By the other hand, the substrate can substantially affect the exciton state in 2D systems. The influence of barrier media on the Coulomb interaction is because of dielectric confinement effect, when there is a strong contrast between the dielectric constants on the boundary of two materials [2, 3].
Because of the two-dimensionality of graphene, charge carriers are affected by the effect of quantum confinement. Moreover, in the case when there is a strong contrast between dielectric constants at the boundary of graphene and the environment, this system is affected also by the effect of the dielectric confinement.
In this research the Coulomb interaction potential in grapheme (bounded by two different barrier media.) is discussed with considering of both, dielectric screening and dielectric confinement effect. By this way, Coulomb interaction potential strongly depends on dielectric constant of barrier materials. So, changing barrier material, we can change the excitonic component of absorption for graphene layer and control some optical properties of system.
The obtained theoretical results are discussed in comparison with the results of an experiment [4] related to the exciton component of the optical absorption spectrum.

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Resistance and surface potential characterization of 2-d materials with atomic force microcopy

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Over the past 30 years, Atomic Force Microscopy has evolved from a microscope to measurejust the surface topography to a wide variety of measurement modes that provides a way to characterize other atomic interactions or physical properties like magnetic field, electric field, nanoscale dissipation processes, thermal conductivity, electrical conductivity, resistance, surface potential, piezoresponse, Young modulus,... Electrical nanocharacterization with AFM has emerged as a powerful tool to map electrical properties at the nanoscale, like surface potential (work function) and conductivity. However, traditional setups in AFM make difficult to obtain accurate and repeteable results over several types of samples.

In this contribution we will show the capabilities new developed AFM modes: High Definition Kelvin Force Microscopy (HD-KFM), ResiScope, Soft-Resiscope and Scaning Microwave that overcome the intrinsic difficulties of electrical nanocharacterization with AFM. This techniques have been applied on a variety of samples of 2-D materials providing high stability, sensitivity and lateral resolution

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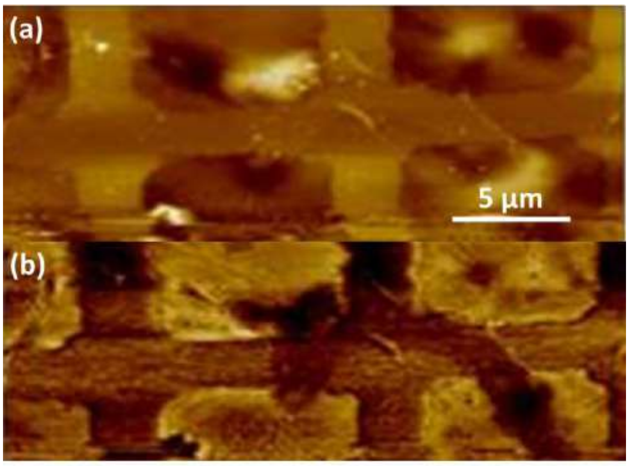

Figure 1: Topography (a) and surface potential (b) of a grafphene membrane suspended over a grid of Si/SiO2.

Bilayer graphene electrooptic modulator with rib dielectric enhancing TE mode confinement

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Double-layer graphene on silicon has been proven to show high performance optical modulation [1] and has shown potential experimental possibilities [2]. We report a novel design of bilayer graphene-on-silicon electro-absorption modulator. Our design involves formation of a rib dielectric structure (SiO_2) within core silicon that pushes the mode towards top graphene layers. Dimensions of the dielectric rib can be *h*/2 and *w*/2, where *h* and *w* are height and width of core Si, respectively. Such waveguide enhances the TE mode confinement and improves light–graphene interaction. The TE and TM modal properties of the waveguide are studied using a Finite element method.

Our design significantly improves the TE mode confinement within graphene layers in a graphene-on-silicon rib waveguide configuration compared to that of a vertical air slot design [3]. This structure is possible to fabricate with existing SOI technology and has CMOS compatibility and on-chip integration.

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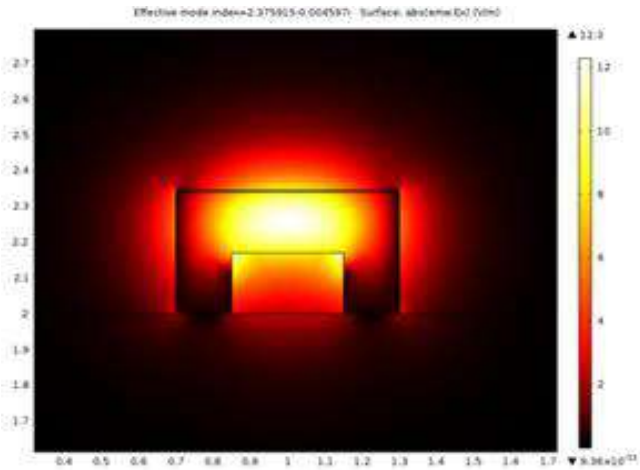

Figure 1: The TE Ex field profile. Waveguide parameters: Si width/height 0.6µm/0.34µm; bilayer graphene 0.69nm; buffer dielectric (Al_2O_3) 0.1µm; rib dielectric (SiO_2) width/height 0.3µm/0.17µm.

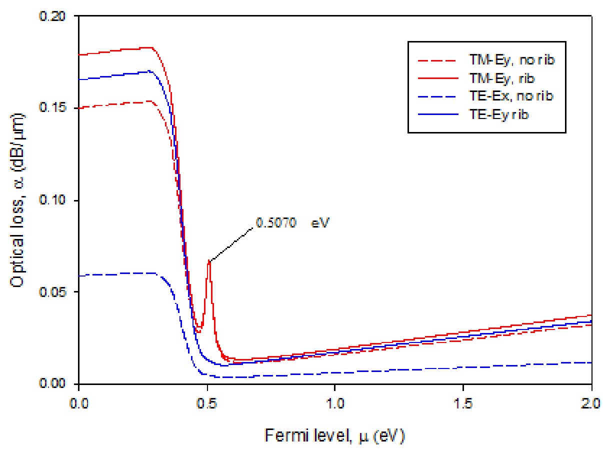

Figure 2: Optical loss (TM, TE) as a function of Fermi level in waveguides with and without SiO2 dielectric rib. Refractive indices of Si, SiO_2 and Al_2O_3 were taken as 3.47, 2.09 and 3.02. In TM plot, a peak at μ = 0.507 eV denotes transition of graphene layer to metallic state, $\varepsilon_{graphene}$ = –0.0839+*j*0.5728, showing epsilon near zero effect in graphene.

Flexible conductive adhesives based on PDMS

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Abstract

The aim of this work is to investigate the formation of flexible and electrically conductive adhesive composites using poly(dimethylsiloxane) (PDMS) and a range of conductive nano and micro particles, [1,2] to investigate the influence of the filler geometry and dispersion on the electrical, dynamic mechanical and thermal properties.
PDMS composites were produced with carbon nanotubes, single-and multi-wall (SWCNT and MWCNT), Indium Tin Oxide (ITO) NPs, mixtures of MWCNT with graphite nanoflakes, and mixtures of MWCNT and Silver (Ag) particles. The composites were prepared on a three-roll mill and the dispersion of the particles in PDMS was observed by optical microscopy and scanning electron microscopy (Figure 1). The combination of particles with different chemistry and morphology for the formation of PDMS composites was studied. Fillers with high aspect demonstrated a positive contribution to the composite electrical conductivity. Conversely, the combination of fillers with different geometry was detrimental to electrical conductivity, except when the fillers had similar chemical composition.
MWCNT/PDMS composites with or without the addition of Graphite flakes presented the higher electrical conductivity results. The storage modulus, E', increased with the filler content and frequency, while maintaining the loss modulus near that of PDMS.
PDMS/MWCNT composites with Graphite nanoflakes showed electrical resistivity as low as 1.5 Ω.cm. The storage modulus, E', increased with filler content while keeping the loss modulus near that of PDMS.
PDMS composites with low concentration of MWCNT and Graphite nanoflakes showed electrical conductivity and excellent mechanical performance, being quite promising for electronic application.

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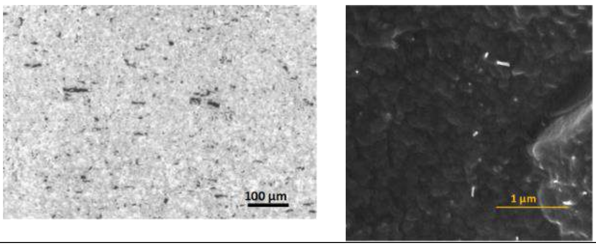

Figure 1: Optical (left) and SEM (right) micrographs of a PDMS composite with 1 wt% MWCNT and 1 wt% graphite nanoflakes.

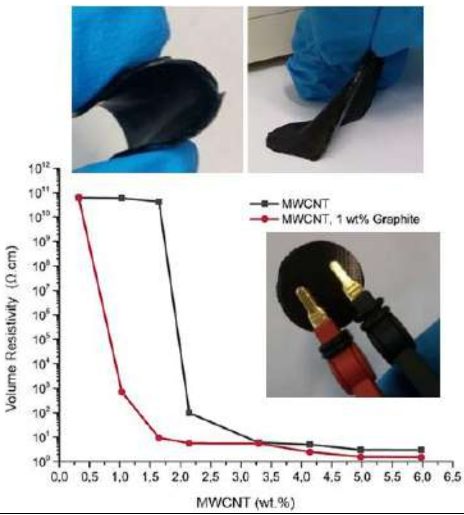

Figure 2: Fotographs of a PDMS/MWCNT/1 wt% Graphite nanoflake composite and percolation curves for PDMS/MWCNT composites and PDMS/MWCNT/1 wt% Graphite nanoflake composites.

Bandgap tailoring of graphene oxide by electric field induced reduction: Applications to photonic micro devices

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Graphene oxide (GO) being a very large bandgap (~3 eV) material behaves as an insulator, that restricts its application in various electronic as well as opto-electronic devices. Reduction of GO leads to removal of oxide functional groups from the graphene layer resulting in reduction of its bandgap with enhancement in its conductivity. There are various techniques adopted for reduction of GO such as chemical, thermal, photo-thermal, photo-catalytic, Laser irradiation etc[1]. All these methods have their own advantages as well as limitations. Recently, voltage induced reduction has been studied to investigate the moisture dependent reduction mechanism[2].

In view of the above, step-wise controlled reduction process of GO and its mechanism need thorough investigation as it has wide applications in the industry of electronics, photonics, biomedical to name a few. In the present work, we have investigated the electric field induced reduction of GO drop-casted film on SiO_2/Si substrate. Time- dependent current-voltage characteristics has been studied and it was observed that on applying constant voltage, the sheet resistance of the film decreases with time. Using this, various reduced GO films have been studied using Scanning tunnelling spectroscopy. It is observed that as time progresses, due to the reduction, the bandgap changes from 3 eV to 0.3 eV. Whereas, the resistance decreases from 10 M Ω to 100 Ω as shown in figure 1 (a). To understand the mechanism, an in-situ absorption of the film was investigated during the reduction process using an indigenously developed diffused reflectance spectroscopy set-up. The differential absorption (ΔA), as shown in fig 1 (b) shows development of a 460 nm band as reduction progresses. The photo response of this partially reduced film has been investigated. A typical photo-response under the illumination of visible light of different intensities are shown in figure 2. The elaborated discussion on the correlation of our observation will be presented.

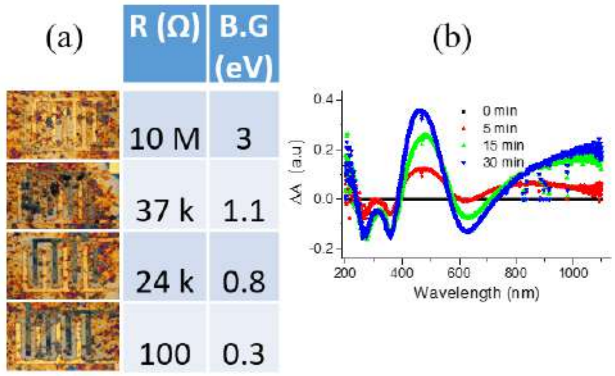

Figure 1: (a) in-situ transient absorption (b) optical images & corresponding B.G of GO at different stages of E.F induced reduction process

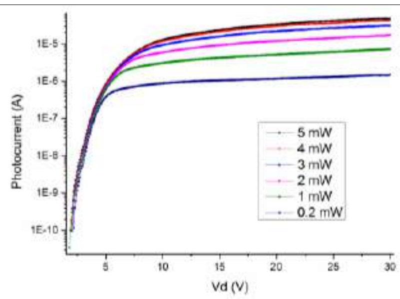

Figure 2: Photo-response of partially reduced GO under broad band visible light at different power.

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Graphene oxide induces sperm release from bovine oviductal epithelial cells by modifying sperm membrane fluidity and binding proteins expression

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Graphene Oxide (GO) has acquired a scattered use in regenerative medicine and biotechnology during the last years. However, data about toxicity on reproduction are controversial. For this reason, our group recently studied the effects of GO on different aspects of swine sperm capacitation, finding out a positive effect in the fertilizing ability of GO treated spermatozoa in vitro, explained by the extraction of cholesterol present in the membrane [1]. With the aim of studying the interaction between GO and spermatozoa in other mammalian species and in a more physiological condition, bovine sperm were co-incubated with bovine oviductal epithelial cells (BOEC) in the presence and absence of GO (1µg/mL). In this in vitro model, the attachment of sperm to BOEC simulate the "sperm reservoir" in the oviduct, where sperm storage, capacitation, fertilization and early embryo development take place [2].
After 30 min of co-incubation with BOEC, spermatozoa were treated 1h with GO, whereupon they were collected and both cells and bound spermatozoa were stained and counted by confocal microscopy, finding a high number of sperm released after GO treatment (data not shown). FRAP analysis was performed on released spermatozoa to evaluate the changes in membrane fluidity, an event directly related to capacitation. The released from BOEC by GO caused an increase in membrane fluidity (Figure 1). To study the expression of the Binder of Sperm Proteins (BSP-1,-3,-5), major proteins of the bovine seminal plasma and keys in the event of capacitation [3], Western Blotting experiments were carried out with the control, unbound and GO-released spermatozoa. A lessen or lacked expression of BSP was seen on GO-released spermatozoa compared to control and unbound sperm (Figure 2).
In conclusion, GO effects were studied in bovine spermatozoa, finding out similar effects to those produced on boar sperm and with an interesting role in the process of capacitation that leads to fertilizing ability acquisition.

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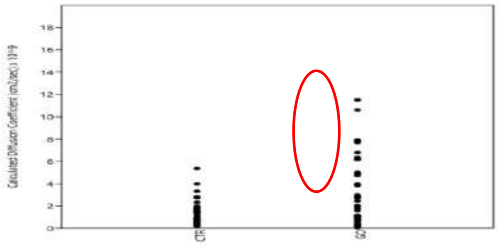

Figure 1: FRAP analysis of GO treated spermatozoa. GO causes an increase in membrane fluidity (p=0.01443).

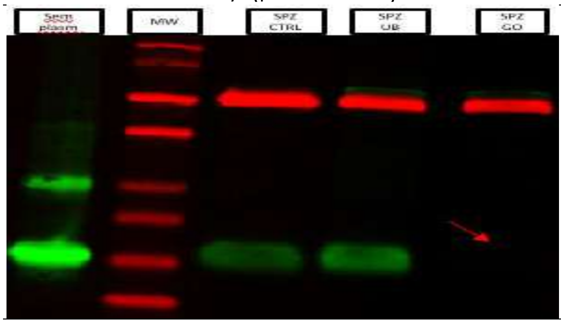

Figure 2: Western Blotting representative experiment shows the lack of BSP-1 (15 kDa) on GO-released sperm (C+: seminal plasma).

Towards the Standardization of Graphene: The Project GRACE

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Nine organizations of different profiles, including National Institutes of Metrology, academic institutions, standardization entities and private companies, has join efforts and are carrying out the Joint Research Project 16NM01 GRACE "*Developing electrical characterisation methods for future graphene electronics*" funded by the European program EMPIR.

The target of the project is comparing and improving methods to characterize electrical properties of graphene and other 2D materials in order to provide input to standardization entities in this field.
The project has two main technical Work Packages which deal with accurate and traceable methods and with high throughput methods, respectively.

WP 1 is devoted to develop accurate testing methods, traceable to the SI. These methods can be contact and contactless methods. Contact techniques include van der Paauw method, in line four probes technique and measurement of S parameters in coplanar waveguide. Contactless methods are, between others, scanning probe microscopy, and microwave and THz based methods.

A basic task of the project is the development of two Good Practice Guides, one for contact methods and the other for contactless techniques.

WP2 deals with high throughput methods, this is, methods with the capability of measuring big quantities of samples in a short time. This is the type of methods typically used in a manufacturing environment. Validation of existing and new methods by comparison with the ones developed in WP1 is another task of the project.

The other two packages of the project are, as usual, one for management and another for Impact creation.

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Figure

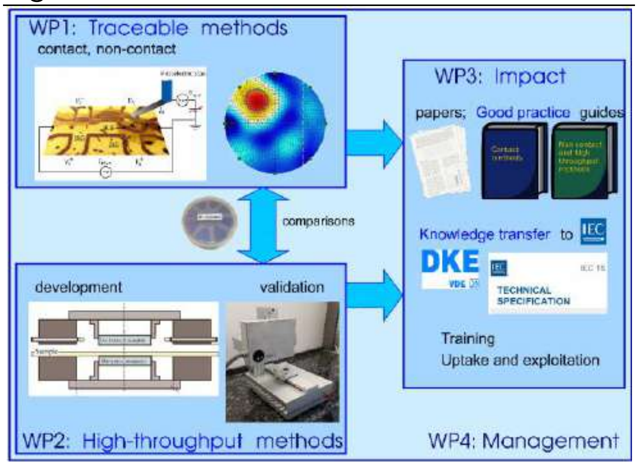

Figure 1: The relationship between the four work packages of the project.

Infrared nano-imaging and spectroscopy on graphene using scattering-type SNOM

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First visualisation and analysis of Dirac plasmons propagating along graphene was realized using the neaSNOM infrared near-field microscope [1, 2] in 2012. Ever since this s-SNOM instrument has routinely been applied for graphene plasmon interference mapping that allows the extraction of local material properties, e.g. conductivity, intrinsic doping and defects. Direct control of propagating surface plasmons on graphene with resonant antennas and conductivity patterns has also been demonstrated using the neaSNOM technology [3, 4].

Additionally, the highly flexible design of the neaSNOM microscope enables a complete new level of correlation microscopy: near-field microscopy in combination with time-resolved measurements [5].

In this presentation, some recent examples of application of the neaSNOM used for graphene research are shown. Carrier relaxation in heterostructures in high-purity graphene [6] as well as photocurrent measurements on graphene will be reviewed [4, 7].

With more than 30 high impact articles published in the last few years on the 'flatland optics', the neaSNOM is the best tool for nanoscale imaging and spectroscopy on graphene.

Furthermore, a technological breakthrough in the field of near-field optics has been achieved with cryogenic near-field imaging and spectroscopy, pioneered by the group of Dimitri Basov [9]. With the new cryo-neaSNOM we extend ambient near-field measurements to the cryogenic temperature range (<10-300 Kelvin) and open a complete new world for nanoscale optical microscopy and spectroscopy [Figure 1]. This technology enables for example the direct mapping of phase-transitions in strongly correlated materials or the detection of low-energy elementary excitations at the surface of solid-state systems.

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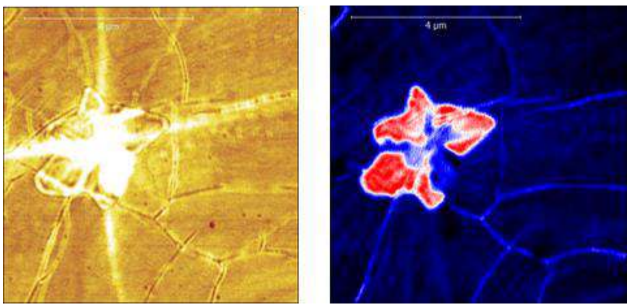

Figure 1: cryo-neaSNOM images of graphene at 8.5 K: a) optical amplitude; b) optical phase.

Proximity Magnetoresistance on graphene induced by magnetic insulators

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Graphene has been attracting great interest due to its fascinating characteristics for development of graphene-based devices in several fields [1,2]. When it is placed on top of a magnetic insulator, it can acquire spin polarization [3]. Evidence of this effect is the emergence of exchange splitting in the graphene band structure reported experimentally [4,5] and theoretically [3,6]. Here we demonstrate the existence of proximity magneto-resistance (PMR) effect in graphene considering magnetic insulator proximity cases reported in Ref. [6]. The PMR calculations were performed using KWANT package [7], for yttrium iron garnet (YIG), cobalt ferrite (CFO), and two europium chalcogenides EuO and EuS [6]. The system studied consisted of two identical proximity induced magnetic regions of width W, length d and separated a distance L_m of a graphene sheet, with its ends connected to two leads [Fig. 1(a)]. We found significant PMR (up to 100%) values defined as a relative change of graphene conductance with respect to parallel and antiparallel alignment of two proximity induced magnetic regions. Namely, for high Curie temperature (Tc) CFO and YIG insulators which are particularly important for applications, we obtained 25% and 80% at room temperature, respectively [Fig. 1(b)]. We also found that the PMR is robust with respect to magnetic region separation, in contrast with its dependency on lengths. Our findings show that it is possible to explore spin polarized currents in graphene with no direct injection through magnetic materials. We acknowledge EU H2020 Programme Graphene Flagship (agreement No. 696656).

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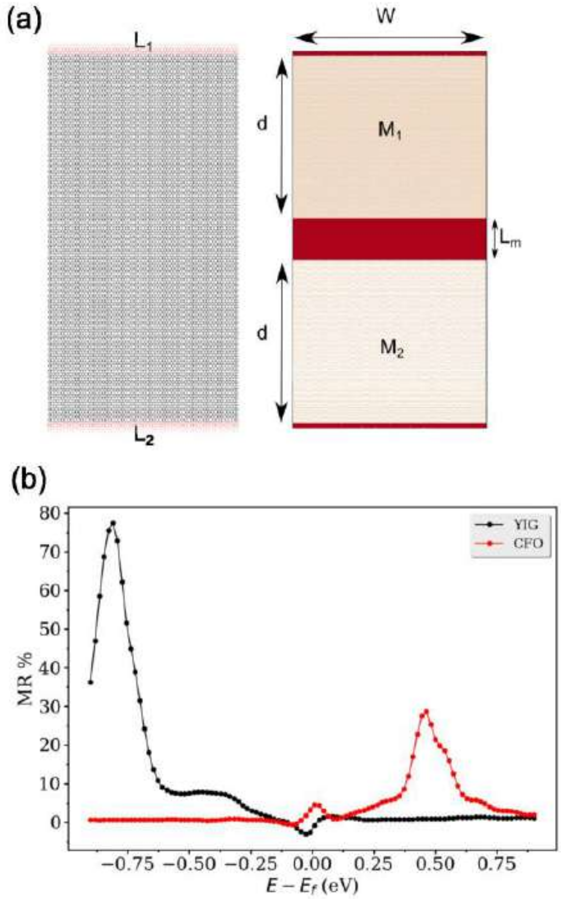

Figure 1: (a) Graphene sheet comprising two proximity induced magnetic regions M_1 and M_2 of width W and length d separated a distance L_m, connected to leads L_1 and L_2. (b) PMR value as a function of energy for YIG and CFO at room temperature in a system with W = 14.8nm, d = 12.8nm and L_m = 1.5nm.

Room temperature electronic localization in a single graphene layer on sapphire by He-ion irradiation

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Atomic disorder along a well-ordered conductive material gives rise to the well-known Anderson localization effect [1]. We use a He-ion beam irradiation with a 1 nm lateral precision to induce the required defects distribution in a single layer of graphene (SLG) to achieve electronic localization at room temperature. An ultra-flat sapphire substrate was used to support the graphene while preserving both its planarity and electronic properties. A 1% carbon defect density [2, 3] was induced line by line, irradiating with the He^+ beam a 100 nm-wide band on the graphene. This is increasing the SLG electrical resistance exponentially from 0.9 to 153 kΩ, demonstrating an overall localization length of 7.8 nm. This resistance build-up was monitored in-situ and in real time by measuring the *I(t)* time dependant current intensity through the SLG flake during the irradiation. For this purpose we used a shadow micro-mask to nanofabricate a metal-graphene-metal micro-junction (Figure 1). We report how the conductance decay during the process varies (Figure 2) which leads to a varying localization length. This is attributed to the local heating of the graphene surface caused by the irradiation. Such behaviour encourages carbon defects migration to the edge of the graphene flake [4], effectively moderating its electrical resistance increase after irradiations.

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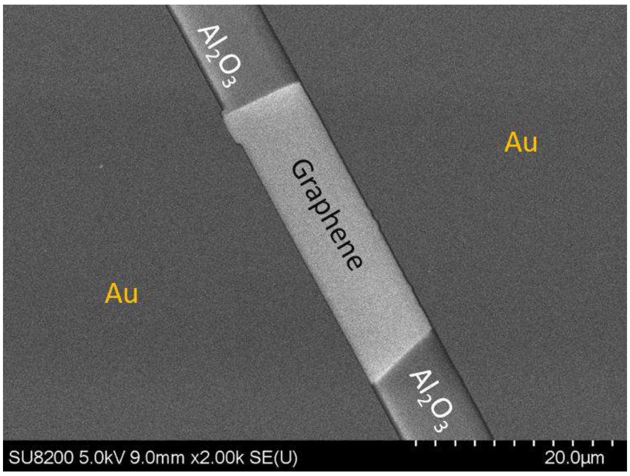

Figure 1: SEM micrograph of the Au-graphene-Au micro-junction.

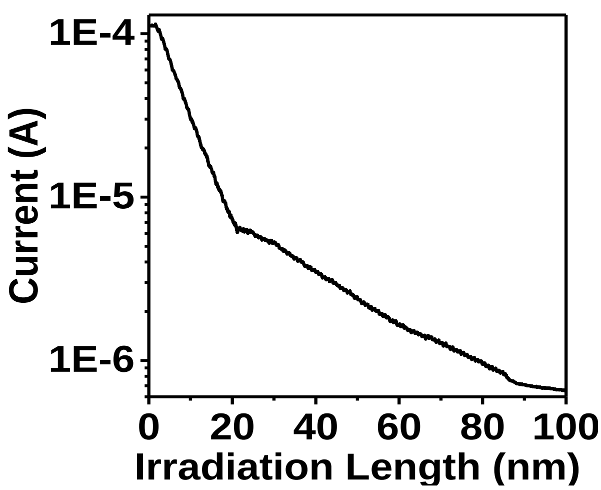

Figure 2: Room temperature electrical current intensity decay during He-ion irradiation of the graphene monolayer in the Fig. 1 junction. Applied bias 100 mV.

GRAPHIN2018 – POSTERS

Atomistic large-scale simulations of transport in ballistic graphene

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Graphene exhibits astonishing mesoscopic effects hosting massless Dirac quasiparticles that can travel with little scattering and behave like light rays [1]. Electrons in graphene devices undergo negative refraction when passing p-n junctions and can be manipulated by external electromagnetic fields, paving the way to a new concept of electronics based on the principles of optics [2]. One interesting perspective is a "2D Dirac fermion microscope" (DFM), where electron guns, tunable lenses, deflectors, and detectors are combined in a graphene "vacuum chamber" to image different types of targets [3]. We perform multi-scale simulations of ballistic graphene devices starting from atoms, combining density functional theory (DFT) and large-scale tight-binding (TB) models in a non-equilibrium Green's functions (NEGF) framework. Using NEGF+TB we reproduce key features of electron transport in a DFM, such as electron beam collimation, deflection and scattering off circular p-n junctions, supporting and extending the results of semiclassical simulations [3]. Pushing towards full atomistic detail, we develop a simple multi-scale approach to locally couple accurate DFT and large-scale TB+NEGF models, based on coupling through a real-space-projected self-energy. We adopt this method to calculate and visualize far-field currents injected from a DFT model of a gold tip in atomic contact with graphene.

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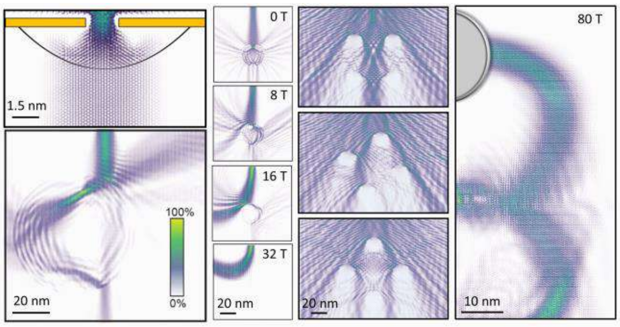

Figure 1: NEGF+TB simulations of a DFM: geometry and bond-currents for various beams and targets [3].

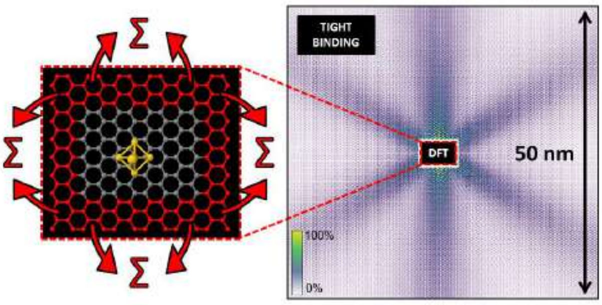

Figure 2: Far-field currents injected from a gold tip in atomic contact with graphene, obtained by coupling DFT with large-scale TB+NEGF models.

Towards characterization of graphene using hybrid metrology approach at LNE

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Graphene attracts LNE's interest for more than 10 years as it is today the most promising material to establish a practical traceability for electrical resistance to the quantum Hall effect [1]. Beyond, graphene can have many innovative applications the development of which needs accurate control of the material properties.

To support the expected disruptions and favour the adoption of the graphene-based technologies by industry, LNE which is the French national metrology institutes has made available its CARMEN platform to provide the different actors with dedicated instrumentation for the accurate characterization of nanomaterials. This platform is integrated in the recently inaugurated LNE Nanotech Institute and gathers experts and relevant instruments for nano-characterization like AFM (Atomic Force Microscope), Metrological AFM to provide traceability of dimensional measurement at the nanoscale to the International System of units SI [2], SEM (Scanning Electron Microscope), Confocal Raman Microscope, SMM (Scanning Microwave Microscope), conductive AFM fitted with Resiscope module, SThM (Scanning Themal Microscope).

As a preliminary work on graphene-based materials, all the available various techniques have been investigated to characterize the same area of a given graphene sample and have been tested for the assessment of the contamination level and the number of layers. The chosen multidisciplinary approach aims at combining several techniques to collect a maximum amount of information on the studied sample and to determine critical parameters through a hybrid metrology approach.

In addition, as national metrology laboratory and internationally recognized testing laboratory, LNE offers its full calibration and measurements capabilities to characterize and validate graphene-based products, from materials to manufactured products (performances, lifecycle, etc)

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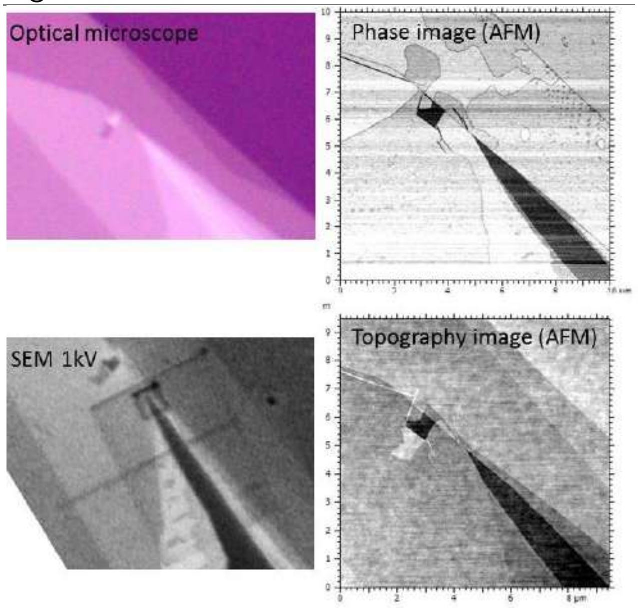

Figure 1: default colocalization on exfoliated graphene using optical microscopy, SEM and AFM

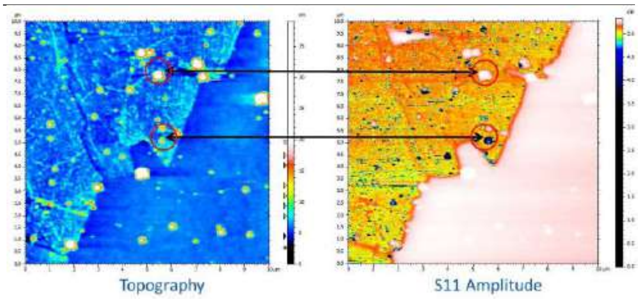

Figure 2: contrast obtained using the SMM at the transition between substrate and CVD graphene layer

Investigation of high frequency performance of hBN encapsulated Graphene Field-Effect Transistors

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Carrier mobility and saturation velocity in graphene are considerably enhanced when this two-dimensional material is encapsulated in hexagonal boron nitride (hBN) [1,2]. This work studies the theoretical limits of high frequency (HF) performance of hBN encapsulated graphene field-effect transistors (GFET). For such a purpose we have implemented a Monte Carlo simulator with the relevant scattering mechanisms, namely, carrier-carrier interaction, intrinsic phonons, remote surface polar phonons and scattering of carriers because of the presence of impurities and defects. Our simulator reproduces the experimental carrier mobility and saturation velocity dependence with carrier concentration [3]. This information is introduced in a self-consistent GFET drift-diffusion simulator that takes full account of short channel effects [4]. HF performance has been studied from a quasi-static small-signal charge-conserving model [5]. This way, direct current and HF are assessed. We have found that HF performance and device stability strongly depends on the bias point. Stability must be guaranteed in circuits targeting signal amplification. We have also observed that the GFETs are more prone to instability when they operate in the negative differential resistance. By using our drift-diffusion simulator, we have found that hBN encapsulated GFETs have the potential to work in the THz range for channel lengths below 200 nm. For comparison purposes we have plotted, in the same graph, the maximum oscillation frequency (f_{max}) that has been reported with Si and InP radiofrequency transistors.
This work is funded by the European Union's Horizon 2020 research and innovation program (No 696656), the *Generalitat de Catalunya* (2014 SGR 384) and the *Ministerio de Economía y Competitividad* (TEC2015-67462-C2-1-R, MINECO/FEDER and FJCI-2014-19643).

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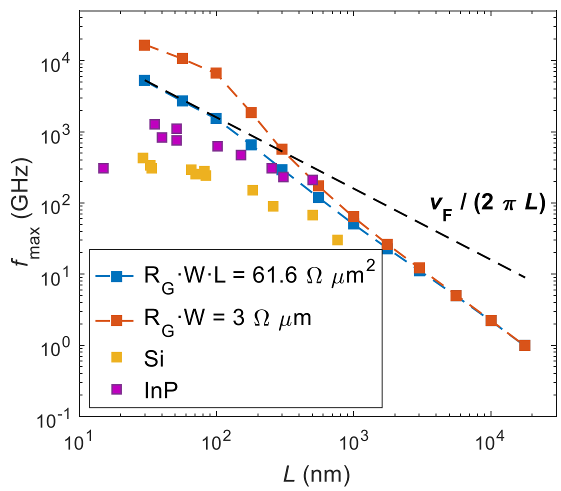

Figure 1: Scaling of simulated f_{max} of hBN encapsulated GFET at drain voltage V_{ds} = 0.1 V. Simulated performance has been benchmarked against state-of-the-art InP and Si technologies. Note that when gate resistance scaling assumption is applied (blue symbols) a sizeable f_{max} improvement is predicted.

Carbon Nanofibers: new additive for the Negative Active Material of Lead Acid Batteries

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Abstract

Lead Acid Batteries (LABs) are in continuous upgrade in order to supply the necessities of the current automotive industry. One of their main objectives is to work in the Micro Hybrid vehicle as power supply source, where LABs must be able to accept the charge of the regenerative braking and to work in High Rate Partial State of Charge (HRPSoC) conditions. In this condition, LABs progressively accumulate lead sulphate ($PbSO_4$) crystals on the negative plates, so their internal resistance increases, causing the battery failure. Addition of carbon materials to the negative plate was one strategy used in order to avoid this sulfation[1, 2].
In this study, Carbon Nanofibers from Grupo Antolin (GANF), previously dispersed, have been used as additives for the negative plates of Lead Acid Batteries (LABs). Four Negative Active Material (NAM) mixtures were prepared: 1 reference mixture (NAM Control) and 3 GANF mixtures (S1, S2 and S3) with different GANF concentrations. These mixtures were used to prepare four types of negative plates, and so 2V/1Ah Lead Acid test cells. Electrical performance of the cells was testing. Capacity, cold cranking ability, charge acceptance, Hydrogen Evolution Reaction (HER) and Partial State of Charge (PSoC) cycle life were analysed among others. Different physicochemical analysis, X-ray diffraction and Scanning Electron Microscopy were carried out for the negative plates.

As a result, carbon nanofibers slightly improved the charge acceptance of the negative plates. Water consumption studies revealed that the selected grade of carbon nanofibres increased HER rate by lowering its overpotential, and its dispersion played a key role in this reaction. However, this gassing increase was lower for GANF in comparison with other carbon materials that are currently used in flooded LABs[3]. Selected GANF increased NAM conductivity during PSoC cycles, leading always to the performance of more than 1000 cycles.

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Reducing Graphene Oxide cytotoxic effects via lipid coating

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Abstract
Toxicity evaluation is a crucial step for the proper use of applications that involve graphene oxide (GO) intravenous administration but the GO circulation time and blood interactions are largely unknown. It is thought that GO causes haemolysis when it interacts with red blood cells but very few studies have been performed to date. We have found that GO can interact with both neutral and negatively charged lipid vesicles. After this binding occurs, neutral membrane vesicles tend to break down and extend over the GO, while vesicles with negatively charges membranes are mainly bound to the GO without disruption. GO also disrupts different cell types when interacts with them, but it has been shown that coatings of chitosan or specific biopolymers can be useful to reduce the GO cytotoxicity [1]. In our study RBC haemolysis and CHO cell lysis have been decreased when GO is previously coated with lipid membranes, particularly with pure phosphatidylcholine vesicles [2].

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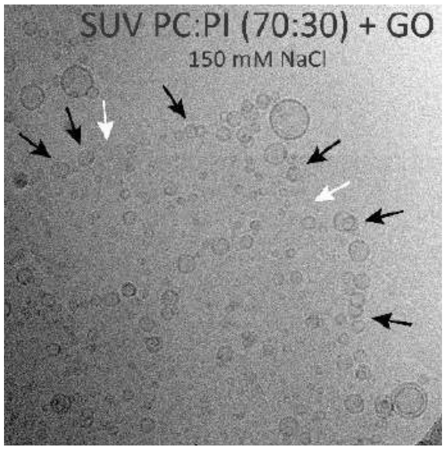

Figure 1: Cryo-TEM imaging of GO and SUV. GO-PC:PI SUV mixture in 150 mM NaCl. GO sheet edges are marked with white arrows; interactions between SUV and planar GO surfaces are labelled with black arrows.

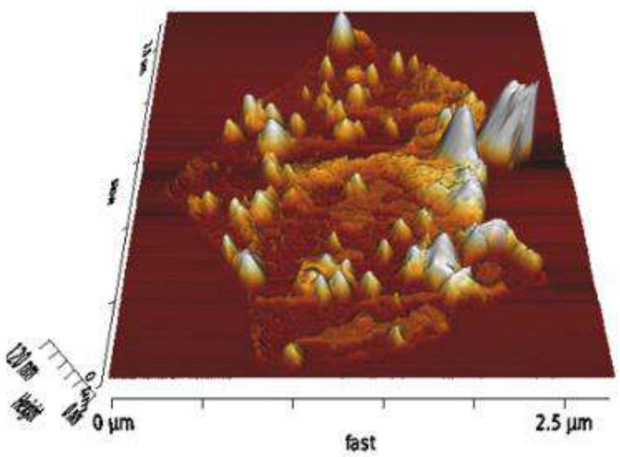

Figure 2: AFM image. 3D reconstruction of the PC:PI (70:30) LUV-GO mixture where extended and semiextended vesicles are seen

A Monte Carlo study of electronic transport in silicene: importance of out-of-equilibrium phonons

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Silicene, the silicon analogue of graphene, is an emerging two-dimensional material with very attractive electronic properties for a wide range of applications [1]. In particular, it could be interesting to develop new nanoelectronic applications using this material due to its direct compatibility with silicon technology and the possibility of inducing an electrically tunable bandgap.

In this work, we study the effect of a phonon out-of-equilibrium population on the electronic characteristics of free-standing silicene. Our ensemble Monte Carlo simulator for 2D materials, that has been applied successfully in previous works to the case of graphene [2], has been used here for the modelling of silicene by incorporating the corresponding band structure and scattering mechanisms as described in [3,4]. The phonon relaxation times were obtained from [5].

The impact of out-of-equilibrium phonons shows to be more important at moderate and high electric fields, provoking a reduction of the saturation velocity and enhancing of energy (Fig. 1). A microscopic study in terms of the electron coupling with phonons and their consequent heating (Fig. 2) reveals an important dependence on the carrier concentration considered. The role of flexural acoustic phonons is also discussed. More results will be presented at the conference.

This work has been supported by the research project TEC2016-80839-P from MINECO and FEDER.

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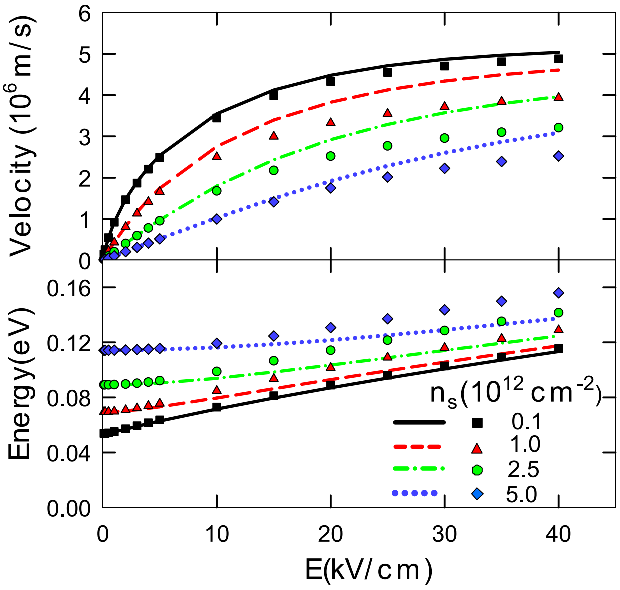

Figure 1: Average drift velocity and energy, as a function of the longitudinal electric field *E*, obtained for four different carrier concentrations (n_s): without (lines) and with (symbols) out-of-equilibrium phonons.

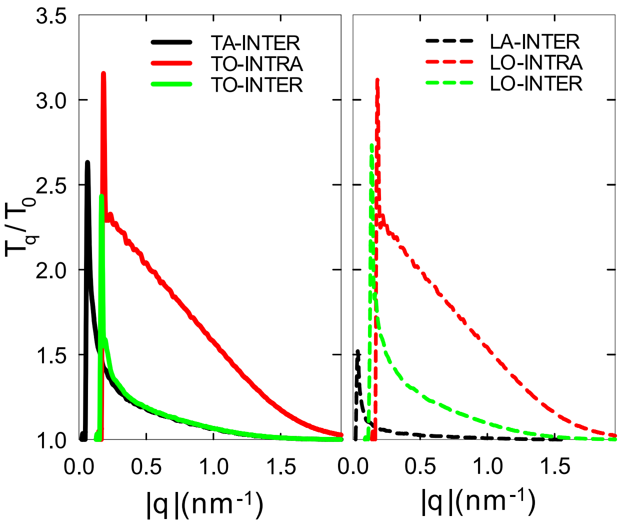

Figure 2: The normalized phonon temperature T_q as a function of the wave vector |q|. T_0 = 300K, E=40kV/cm, n_s=5x10^{12}cm^{-2}.

Electrostatics of atomically thin lateral heterojunctions

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The increasing technological control of two-dimensional materials has allowed the demonstration of 2D lateral junctions, which display unique properties that might serve as the basis for a new generation of 2D electronic and optoelectronic devices. Here we report the investigation of 2D lateral junction electrostatics, which differs from the bulk case because of the weaker screening, producing a much longer transition region between the space charge region and the quasi-neutral region, making inappropriate the use of the complete-depletion approximation[1-3]. For such a purpose we have developed a method based on the conformal mapping technique to solve the 2D electrostatics, which is widely applicable to any kind of junctions, giving accurate results for even large asymmetric charge distribution scenarios. The technique provides a suitable tool to investigate the depletion width, the electrostatic potential, electric field, and surface charge carrier distribution in dependence on the chemical doping densities and dielectric constant of the surrounding environment (see Fig. 1). The proposed technique could be helpful for 2D lateral junctions design and as a benchmarking for further compact model development.

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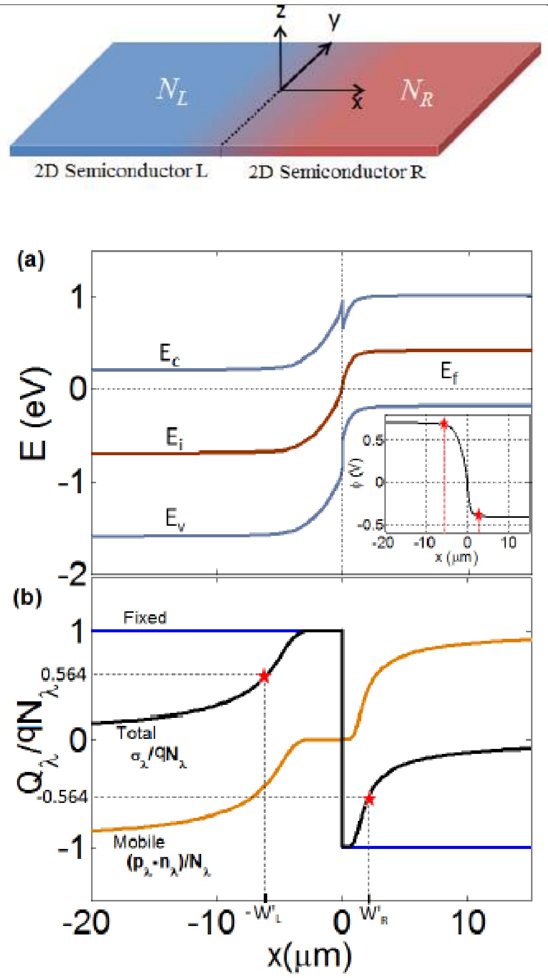

Figure 1: (Top image) Sketch of the 2D junction considered in this work. (Bottom image) Electrostatics of an exemplary 2D lateral Np heterojunction. (a) Energy bands and electrostatic potential (Inset); (b) Surface charge density relative to the fixed charge at both sides of the junction. Red stars in (b) and inset of (a) indicate the relative charge and electrostatic potential at the edge of the depletion widths, respectively.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 696656, and the Ministerio de Economía y Competitividad of Spain under grant TEC2015-67462-C2-1-R (MINECO/FEDER).

Low frequency noise modelling in single-layer graphene FETs

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In this work, a new analytical model is proposed for low frequency noise (LFN) in single layer graphene FETs (GFETs). The model is derived based on a methodology proposed for Metal Oxide Semiconductor FETs (MOSFETs) where the device channel is divided into elementary sections[1]. It is then implemented considering the chemical potential-based compact model of Ref. 2. LFN fluctuations at each local section are modeled by a local current noise source as shown in Fig. 1. Data from liquid-gated GFETs[3] accurately validate the proposed model at different device dimensions and operating conditions. Carrier number (ΔN) and mobility fluctuations (Δμ) effects are the main phenomena that generate LFN in electron devices. We demonstrate that both contribute to the bias dependence of LFN in GFETs especially near the Dirac point, where the well-known M-shape[4] is also observed in our data. Fig. 2 illustrates that the residual charge r0 is responsible for the M-shape when ΔN fluctuations dominate. The higher the residual charge, the more intense the M-shape predicted by the ΔN model. The Δμ model, however, follows a Λ-shape and its contribution can be significant near the Dirac point. A slight increase of the minimum of LFN at Dirac point when V_{DS} increases is caused by the graphene charge inhomogeneity, which is taken into account by the model.

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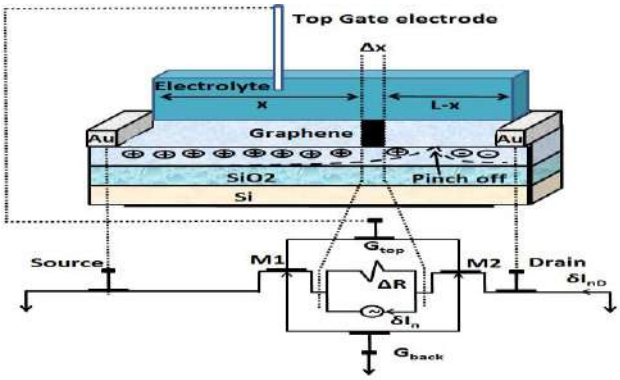

Figure 1: Device cross section with the equivalent circuit of a local current noise contribution to the total noise[1].

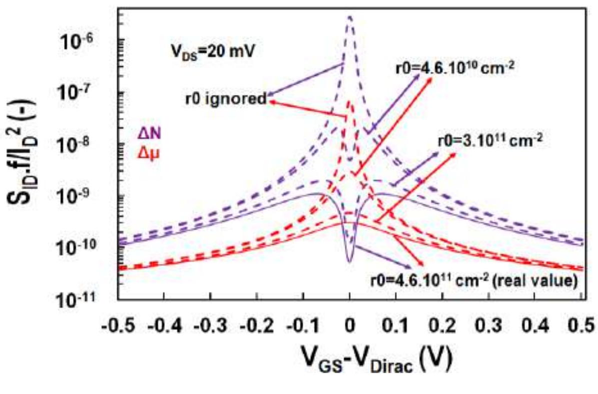

Figure 2: *ΔN* and *Δμ* effects at $V_{DS} = 20\ mV$ for four different values of residual charge (*r0*).

This work was funded by the Ministerio de Economía y Competitividad under the project TEC2015-67462-C2-1-R and the European Union's Horizon 2020 research and innovation program (grant agreement No 696656).

Modeling of Metal-Insulator-Graphene-Metal diodes targeting RF applications

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Metal-insulator-graphene-metal (MIGM) diodes for radio-frequency applications have been recently demonstrated [1]-[2]. Its rectification capability relies on the bias dependent Schottky barrier height, which can be strongly modulated due to the work-function tunability of graphene. Excellent figures of merit (FoM) have been reported so far for this diode, including high on-current density, high asymmetry, strong maximum nonlinearity and large maximum responsivity outperforming several of such FoMs of metal-insulator-metal (MIM) diodes.

Here in this work a large-signal model of the vertical MIGM device (which scheme is shown in Fig. 1) has been developed, with the goal of simulating both static and dynamic regimes of complex circuits based on this technology. So, as a first step, we have implemented a compact model of the Schottky barrier height, which is based on the diode electrostatics (see Fig. 2a). Next, a model for the diode static current has been developed taking into account the carrier injection between a bulk (3D) metal and 2D graphene channel [3], [4] (Fig. 2b). Here a Dirac-Schottky or Dirac-thermionic emission has been assumed to take place, in which carriers are thermally excited over the tunnel barrier at the electrode/insulator interface. The dynamic response of the diode has been determined by adding an intrinsic capacitance, which is formed by the series combination of the geometric oxide capacitance and the quantum capacitance of graphene. The model has been implemented in Verilog-A, a language suited to circuit simulators.

Acknowledgements

This work was funded by the *Ministerio de Economía y Competitividad* under the project TEC2015-67462-C2-1-R and the European Union's Horizon 2020 research and innovation program (grant agreement No 696656).

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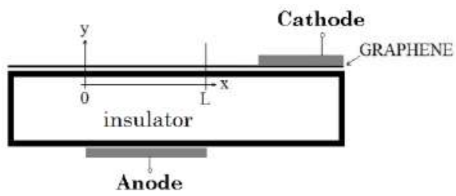

Figure 1: Cross-section of the vertical MIGM diode considered in this work.

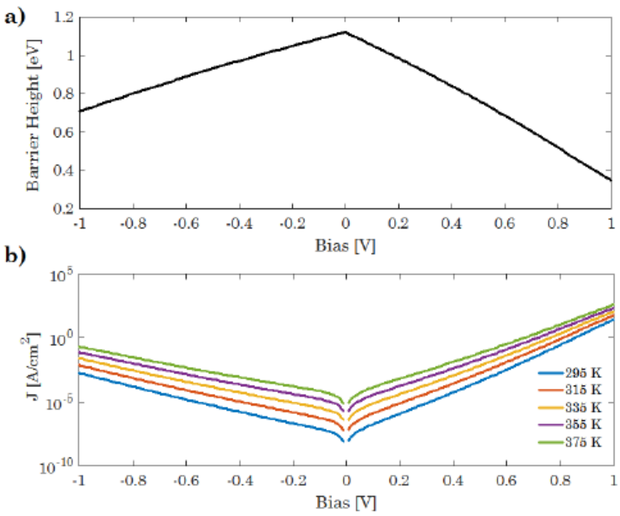

Figure 2: a) Schottky barrier height for electron transport and b) Current density –voltage (*J-V*) curve of a MIGM diode for different temperatures.

MASTRO – Intelligent bulk Materials for a Smart Transport sector

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Abstract

MASTRO is an EU project (NMBP-04-2017) leaded by Acciona Construcción and formed by a consortium of 16 partners, including universities, research centres and large and SMEs companies. The objective of the project is to develop intelligent bulk materials for smart applications in the transport sector incorporating several self-responsiveness properties to increase consumer safety, component life-span and performance, while reducing maintenance and manufacturing costs and greenhouse gas emissions.
Self-responsiveness functionalities will be achieved by incorporating electrical conductive nanomaterials like carbon nanotubes (MWCNTs) and graphite-based nanomaterials into smart lightweight polymer composites, thermosetting and thermoplastics materials, as well as with asphalts and concrete formulations. The self-responsiveness functionalities will include: self-sensing, self-deicing, self-curing, self-healing and self-protection, all based on three physical phenomena: piezoresistivity, Joule's first law effect and electrostatic dissipation.
The functionalized intelligent bulk materials will be incorporated into different critical transport sector components such as wing leading edge in aircrafts, car bumpers and pavements, and demonstrated under relevant conditions at prototype level for the aerospace, automotive and transport infrastructure sectors.

Figures

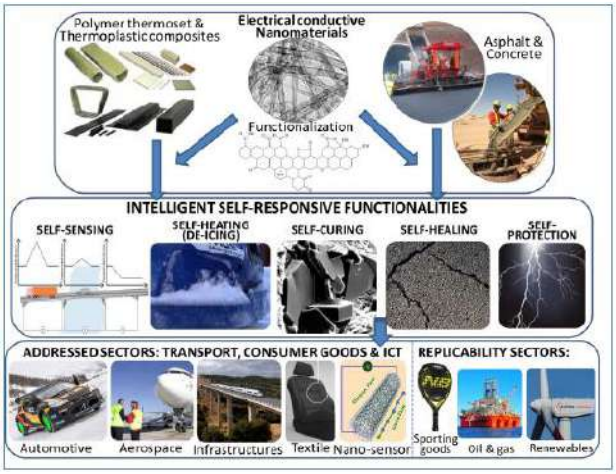

Figure 1: MASTRO project objectives. From materials through self-responsive technologies to the addressed sectors

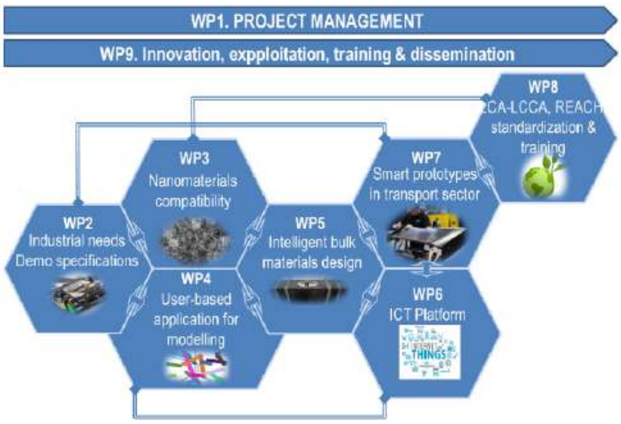

Figure 2: Project structure and interaction between Work Packages

Acknowledgements. This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement N°760940.

Environmentally-friendly graphene-based waterborne polyurethane nanocomposites

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Abstract

The environmental awareness has been one of the reasons of increasing research and development of eco-friendly green synthesis routes for many different applications. Among others, waterborne polyurethane (WBPU) dispersions present the advantage of being synthesized by a solvent-free method, which implies low organic compound levels and non-toxicity comparing with conventional solventborne polyurethanes [1]. Furthermore, these dispersions provide the opportunity of incorporating water dispersible nanoentities enhancing or even providing additional properties. In this context, the addition of graphene has focused attention considering the reinforcing effect providing conductive properties to the final material.

In general, graphene oxide nanoentities are chosen for this type of dispersions, taking into account that the introduction of oxide functional groups favor their dispersibility in water [2]. Nevertheless, the functional groups can also act as defects points in the surface of graphene, decreasing their conductivity capacity [3]. Thereby, alternative routes for the incorporation of hydrophobic graphene to waterborne systems have become a new challenge towards the preparation of high conductive materials.

In this work, the challenge of dispersing graphene into water has been addressed through the use of biomass derived surfactants, for the subsequent preparation of nanocomposites which have been broadly analyzed in terms of thermal, mechanical, thermomechanical, morphological and conductive properties.

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Acknowledgments

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Figures

Figure 1: Graphene-based nanocomposite dispersion and film images

Repeatable and non-destructive transfer of large-area graphene onto arbitrary substrates

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Synthesis of graphene by chemical vapour deposition (CVD) on commercially-available copper foils [1] is a promising and economical route towards producing high quality, continuous sheets of graphene, and is being rapidly scaled to industrial volumes of production [2]. However, transferring such large quantities of graphene onto target substrates in a reproducible manner accounts for a significant portion of the production costs [3]. Here, we demonstrate a simple method for transferring large areas of graphene onto arbitrary surfaces using a commercially available polymer foil as a carrier substrate. The method provides a non-destructive technique to transfer graphene that is also economical, reproducible, and scalable – we have demonstrated graphene transfers at scales of up to A4 sheets of paper – and can also be used to transfer hexagonal boron nitride from various catalyst substrates.

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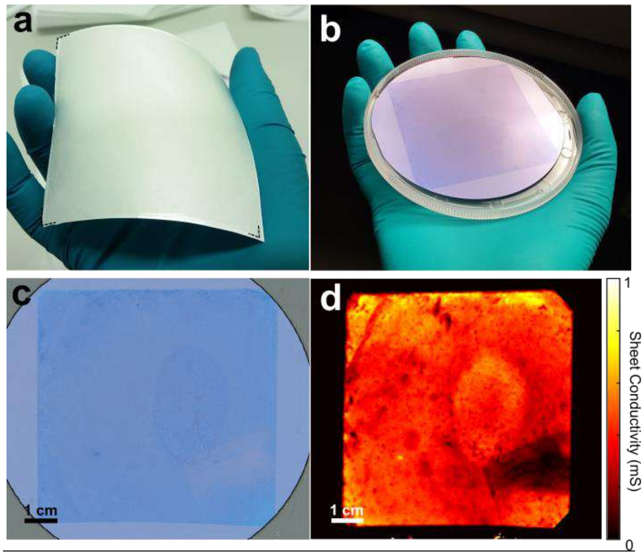

Figure 1: (a) Photograph of 10 cm x 10 cm polymer carrier foil with graphene transferred on top, (b) photograph of graphene in (a) transferred onto a 4'' 90 nm SiO_2/Si wafer, (c) optical micrograph and (d) terahertz time-domain spectroscopy map of sheet conductance of transferred film in (b).

Enhancement of Gas Barrier and Mechanical Properties in Polymer Nanocomposites using 2D Materials

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Together with their exceptional electrical, thermal and mechanical properties, graphene is also being explored for gas barrier applications in packaging, chemical processing and transportation industries. Its impermeable structure and high aspect ratio create a tortuous path for gas molecules within the polymer matrix[1], thus making it difficult for gas to diffuse and get transported across the membranes. In this study, we investigate the effect of different aspect ratios of graphene on the gas barrier properties of the polymer nanocomposites (PNCs), where the nanofillers have been incorporated. Poly methyl methacrylate (PMMA) PNCs were prepared by solvent casting technique, using different types of graphene powders dispersed into acetone and chloroform, with the help of sonication. The as prepared PNCs demonstrated significant improvements in the gas barrier properties of the polymer matrix, depending on their aspect ratios, and in particular, a reduction of 72 % in the gas permeability was observed when graphene flakes with the highest aspect ratio was used. The oxygen transfer rate (OTR) was reduced from 232 mL/m^2.day for the pristine PMMA films, to 65 mL/m^2.day at 3.0 wt.% graphene mass loading. This can be attributed to the good dispersion of the graphene flakes into chloroform solvent[2] and packing of the graphene flakes into PNCs. Likewise, mechanical properties (Young's modulus) of the as prepared PNCs were improved at similar mass fractions, making the PNCs more resistant to deformations. The prepared nanocomposites have been also characterized using SEM, TEM and Raman spectroscopy.

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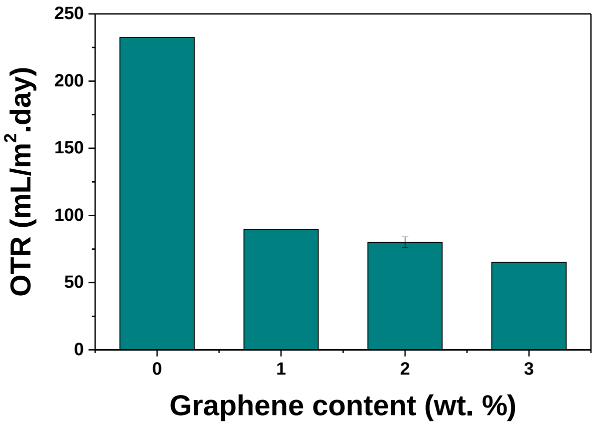

Figure 1: Effect of graphene mass contents on gas barrier properties (oxygen transfer rate) of the PMMA nanocomposites. Here 0 wt. % indicates a pristine PMMA film.

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Nanostructures for Phononics

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Thermal management has become an important field due to increasing importance of thermal properties in devices with reduced dimensions [1]. Confinement of acoustic phonons was experimentally demonstrated in freestanding silicon membranes in early 2000 [2], and this finding has led to a number of papers in which the effect of dimensions on the behaviour of phonons has been investigated. In thin membranes the velocity of phonons slows down [3] and the dispersion can be further affected by strain [4,5], and especially the surface structuring has a significant effect on the thermal conductivity [6]. The reduced thermal conductivity enhances considerably the thermoelectric properties of silicon and enables realisation of new types of thermal detectors [7]. Nanostructured silicon also opens new possibilities in optomechanics due to enhanced nonlinearity of the material [8]. In this talk, we will discuss some of the main outcomes in the field of nanophononics and the future prospects.

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Driving Plasmon-Enhanced Molecular Spectroscopy to the Atomic Scale

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Electronic transitions and vibrations of molecules can be more effectively excited under the action of optical resonators which improve the interaction between light and matter. Among the variety of optical resonators, plasmonic cavities emerge as a special type which allows for reduction of the electromagnetic effective mode volumes down to the nanoscale, thus allowing to bring molecular spectroscopy such as fluorescence or Raman scattering to extreme regimes of resolution and interaction strength.
Furthermore, atomic-scale morphological features in plasmonic cavities produce the ultimate confinement of light, setting sub-nanometric access and control of single-molecule electronic excitations as well as nanoscale molecular optomechanics. To describe the interaction between light and matter at this ultraconfined level, quantum theoretical frameworks which involve methods of condensed matter physics, quantum chemistry and quantum optics are needed.

Furthermore, the inhomogeneous plasmon field distribution in the proximity of a metallic nanoantenna where a molecular emitter is located, provides a special situation in cavity optics which requires the emitter to be studied beyond the dipolar approximation, contrary to commonly considered in molecular fluorescence. To address the limitations of point-dipole approaches we perform full quantum chemistry calculations of electronic transitions in organic molecules of interest located in plasmonic cavities which reveal quantitative and qualitative differences in the coupling strength and emission dynamics with respect to point-dipole approaches.
A similar situation can be found in Raman spectroscopy of similar molecules under the influence of inhomogeneous plasmonic fields. Such fields break selection rules and improve the strength of optomechanical interactions, producing nonlinear Raman signals.
The use of extreme plasmonic fields as shown here provides a new platform to push light-matter interactions in molecular spectroscopy to the atomic scale limit.

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Figures

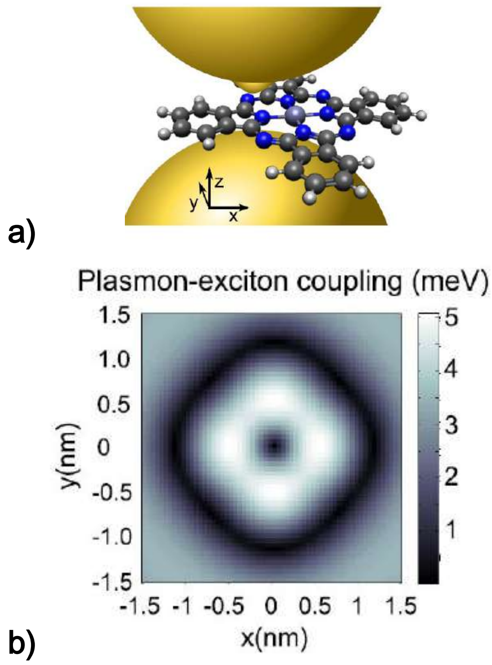

Figure 1: (a) Schematics of an organic molecule (ZnPc) in a plasmonic cavity. (b) Spatial map of the plasmon-exciton coupling strength for the situation depicted in (a). The plasmonic cavity scans the molecule horizontally (XYplane).

Correlating the Structure of 2D Materials with Their Catalytic Activity

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Nanostructures are one of the most extensively researched systems in nanoscience. Various materials are investigated due to their size dependent optical properties or due to their enhanced functionality as catalysts. Although they have been extensively researched for a few decades now, even today new fabrication routes are still explored to improve properties and to gain precise control of their structure. While reports on the optical properties of single particles are available, the quantitative characterization of atomic order on a single particle level and the growth mechanism that resulted in that specific rearrangement, are still generally missing. The majority of characterization procedures are performed on ensembles that average properties and may hinder the understanding of fundamental aspects in the colloidal synthesis.

Here, the formation of ternary compounds of transition metal di-chalcogenides (TMDs) by wet chemistry will be described. Specifically, the doping of TMDs with other transition metals and the impact it has on their catalytic properties for hydrogen production will be presented. The growth mechanism of nanoflowers nanostructures of TMDs was revealed using electron tomography. This growth mechanism allows for facile doping of the materials by adding the dopants either at the beginning or at the end of the reaction, thus forming a homogenous material or a graded one. We have used this approach to dope MoS_2 with Ru, and significantly improving its catalytic activity towards hydrogen production. In addition, we prepared many ternary compounds, and correlated the composition with catalytic activity.

In addition, we have surveyed the structural features of various hybrids in order to correlate them with the catalytic activity. Typical defect motifs will be shown and discussed. This work aims at correlating the atomic-scale structures with the catalytic activity, and for that goal to be achieved, there is a need to understand the dopant sites and the atomic scale arrangement within the MoS2 lattice. The use of high resolution electron microscopy with other characterization methods allows first the understanding of the structural features of the materials and thereafter it will serve to understand the origin of catalytic activity.

Figures

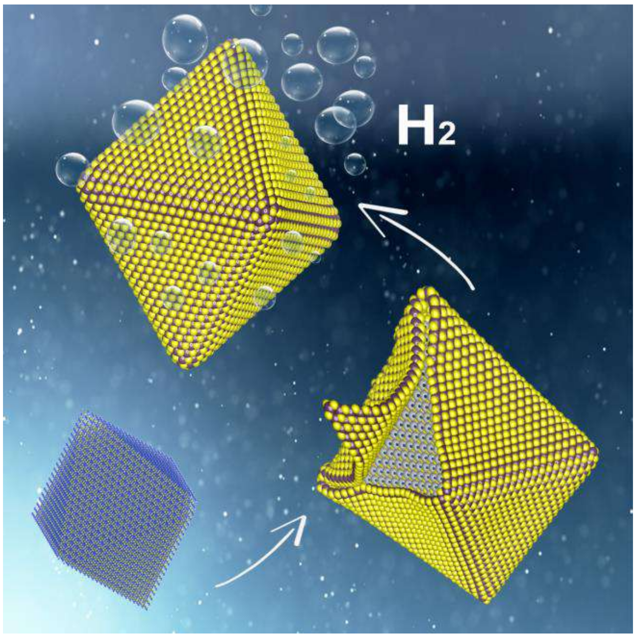

Figure 1: Activating the basal plane of MoS_2 for the hydrogen evolution reaction by the use of a $Cu_{2-x}S$ template

Probing mode connectivity in photonics using two classical or quantum nanosources

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Probing unambiguously the transition from diffusion to localization of light in multiple scattering media remains an open issue. We introduce the mode connectivity, an observable defined from the cross and local densities of states [1], as a measure of the number of eigenmodes connecting two points at a given frequency in a structured environment. An important feature of the connectivity is that it takes a value 1 when the two observation points are connected by exactly one mode, and vanishes in the absence of modes connecting the observation points. In a disordered medium, this property can be used to discriminate between diffusive transport or localization. Indeed, in the diffusive regime, the eigenmodes overlap both in frequency and space. At a given frequency, eigenmodes are spatially extended, and any point in the medium is covered by a large number of modes. Conversely, in the localized regime, at a given point and for a given frequency, no more than one mode has a non-negligible contribution. In this work, we support this qualitative picture is by numerical simulations of light scattering in two dimensions, and show that the connectivity discriminates between the diffusive and the localized regime. For practical implementation, a strategy could rely on the measurement of intensity fluctuations in the emission by two nanosources placed inside the medium (or close to its surface). For both classical dipole emitters [2] and quantum single-photon sources [3], we show that the connectivity is encoded in the second-order coherence of the emitted light, providing clear signatures of the presence of localized modes (Fig. 1) [4].

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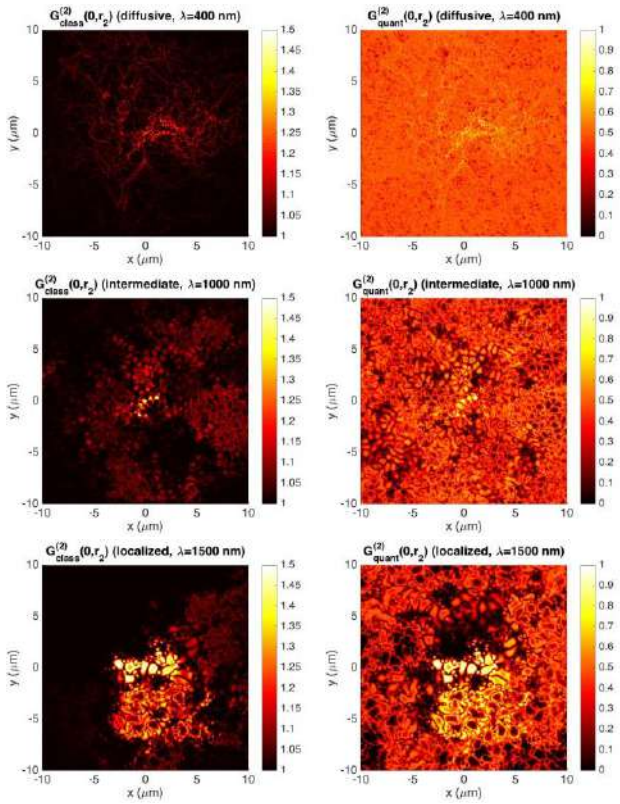

Figure 1: Calculated maps of the second-order coherence function G(2) of the light emitted by a dipole source placed at the center of a 2D disordered medium, while the second source is scanned inside the medium. Left column: Classical dipole sources. Right column: Quantum single-photon sources. Top row: Diffusive regime. Middle row: Intermediate regime. Bottom row: Localized regime.

Super-Planckian Far-Field Radiative Heat Transfer

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Understanding heat exchange via thermal radiation is key for many areas of science and engineering [1]. Radiative heat transfer between closely placed objects, with separations smaller than the thermal wavelength λ_{Th} (~10 μm at room temperature), is attracting a lot of attention because of the possibility to overcome the classical limit set by Planck's law [2-4]. However, in the far-field regime, when gaps are larger than λ_{Th}, thermal radiation is supposed to be well understood and no super-Planckian heat transfer has ever been reported.

In this talk, I will present our recent theoretical work that demonstrates that the far-field radiative heat transfer between objects with dimensions smaller than λ_{Th} can overcome the Planckian limit by orders of magnitude. In particular, I will illustrate this phenomenon with the case of suspended pads made of polar dielectrics like SiN [5]. These structures are widely used to measure the thermal transport through nanowires and low-dimensional systems and can be employed to test our predictions [6]. Moreover, to explore the limits of the violation of Planck's law in the far-field regime, I will also present our results for the super-Planckian far-field radiative heat transfer between 2D materials such as graphene and black phosphorous [7]. The ensemble of our results shows the dramatic failure of the classical theory to predict the far-field radiative heat transfer between micro- and nano-devices.

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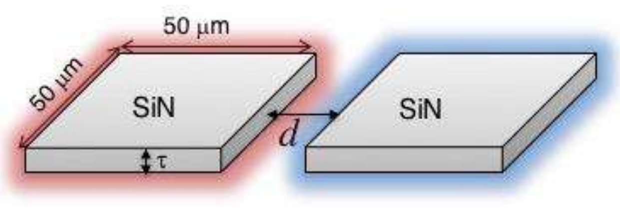

Figure 1: Far-field radiative heat transfer between two micron-sized suspended pads made of SiN.

Polaritons for Chemistry and Materials Science

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Exciton transport plays a crucial rule in natural phenomena such as photosynthesis and in artificial devices such as organic solar cells, but is inefficient in many organic materials. We will discuss how the formation of collective polaritonic modes can dramatically enhance the efficiency of exciton transport when the molecules are strongly coupled to an electromagnetic mode [1]. This effect can be exploited to either "harvest" and direct excitations to specific positions by tuning the spatial distribution of the EM mode [2] or to extend the spatial range of the Forster energy transfer process [3]. We then show that in systems with a discrete EM mode spectrum, strong-coupling-enhanced exciton transport can proceed through "dark" modes that have no photonic component, but which nonetheless acquire a delocalized character in the strong-coupling regime [4].

In the second part, we discuss the influence of strong coupling on internal molecular structure and chemical reactions. While most models of strong coupling are based on simple two-level models, pioneering experiments have shown modifications of chemical reaction rates under strong coupling [5]. In order to address this mismatch, we have developed a first-principles model that fully takes into account both electronic and nuclear degrees of freedom [6]. We will first discuss the applicability of the Born-Oppenheimer approximation, which is challenged by the introduction of the new intermediate timescale of energy exchange between the molecule and the field. Based on these findings, we then show how photochemical reactions such as photo-isomerization can be almost completely suppressed under strong coupling [7]. Finally, we show how polaritons can also lead to the formation of a polaritonic ``supermolecule'' involving the degrees of freedom of all molecules, opening a reaction path on which all involved molecules undergo a chemical transformation [8].

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Quantum plasmonics

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In this talk, we report experiments aiming at exploring the physics of surface plasmons in the single plasmon regime. In other words, we revisit quantum optics using surface plasmons: tests of the wave-particle duality of surface plasmons [1], two photon interference on a lossy beam splitter[2], and the observation of entanglement between a photon and a plasmon[3]. In order to perform these experiments we have designed and built a plasmonic chip shown in Figure 1. The experiments confirm the wave-particle duality of the surface plasmons and the possibility to entangle a photon and a plasmon. New effects were discovered when illuminating the beam splitter with two plasmons, one on each channel, in the so-called Hong-Ou-Mandel configuration.

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Figures

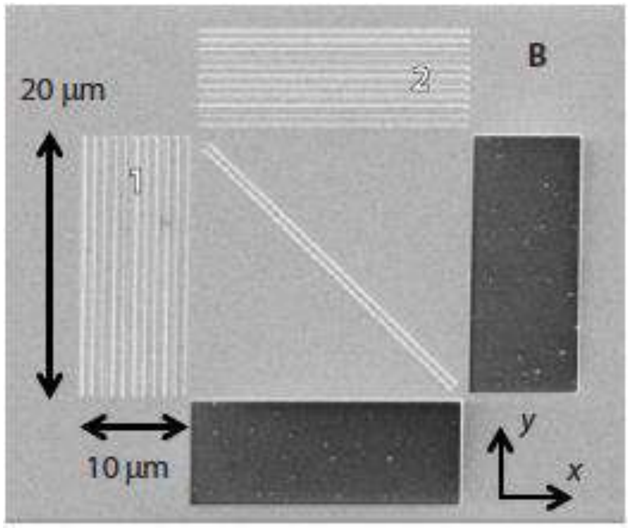

Figure 1: Photograph of the plasmonic chip. Two gratings (1 and 2) are used to couple noramlly incident photons into surface plasmons polaritons. The grooves along the diagonal serve as a beam splitter for surface plasmons. After transmission or reflection by the beam splitter, the surface plasmons propagate towards the slits where they are coupled iinto photons.

Hybrid optoplasmonic and nanomechanical sensor for proteomics

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Blood contains an unknown treasure trove of protein biomarkers that will be crucial for early detection of cancer or other fatal diseases and for personalized medicine. Current proteomic technologies have developed rapidly during recent years with improved limits of detection and multiplexing capability. Unfortunately, these developments together major investments and large international efforts have not resulted into new useful protein biomarkers. A fundamental reason for this dismal progress is the extraordinary complexity of the human plasma that comprises more than 10,000 protein species with known concentrations ranging more than 10 orders of magnitude. It is expected that biomarkers for early cancer or infectious disease detection are at concentrations of at least one million times lower than blood proteins, which is well-below the bottom of the current detection limits in proteomics. Although, the analytical capability of proteomic technologies is rapidly improving, there is an urgent need of new ultrasensitive technologies that can access to the deepest part of the human plasma proteome[1].

In this talk I will present a hybrid nanomechanical and optoplasmonic nanosensor we have developed recently. The immunoassay comprises a sandwich assay that involves the recognition of a protein biomarker first by a surface-anchored antibody and second by an antibody free in solution that recognizes a free region of the captured biomarker. This second antibody is tethered to a gold nanoparticle that acts as mass and plasmonic label. The double signature is detected by means of a silicon cantilever that serves as mechanical resonator for 'weighing' the mass of the captured nanoparticles; and as optical cavity due to the two reflective opposite surfaces, that boosts the plasmonic signal from the nanoparticles. Merging mechanical and optical transduction schemes in the same platform provides remarkably superior performance and higher reliability than devices based on a single transduction scheme. The concept was demonstrated with two cancer biomarkers, the carcinoembryonic antigen (CEA) and the prostate specific antigen (PSA). An unprecedented detection limit of 1×10^{-16} g ml^{-1} in serum was achieved with both biomarkers[2], which is at least seven orders of magnitude better than that achieved in routine clinical practice. Very recently the hybrid nanosensor was also challenged for the early detection of HIV-1 in human serum [3]. Again, the limit of detection achieved was of 10×10^{-16} g ml^{-1}, which is equivalent to only one virus in 10 mL of blood. More importantly, the immunoassay confidence is of 95%. Due to the ultrasensitivity of our nanosensor the undetectable phase after HIV infection could be reduced to just one week and the dreamed early detection of cancer could be a reality in the future. Moreover, the presented hybrid sensor is simple and affordable, and thus it can be easily implemented in health systems.

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Selective Photoinduced Eradication of Cancer Cells by DARPin-Gold Nanoparticle Conjugates

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We have demonstrated [1] that the designed ankyril repeat protein (DARPin) _9-29, which specifically target human epidermal growth factor receptor 2 (HER 2) overexpressed in breast cancer cells, binds tightly to gold nanoparticles (GNPs) forming a coating layer around the particle (see Fig. 1). Binding of the protein strongly increase the colloidal stability of the particles. The results of molecular dynamics simulations showed that approximately 35 DARPin _9-29 molecules are bound to the surface of a 5 nm GNP and that the binding does not involve the receptor-binding domain of the protein. The confocal fluorescent microscopy studies showed that the DARPin-coated GNP conjugate specifically interact with the surface of human cancer cells and enter the cells by endocytosis. Illumination of the nanoparticle-treated cells at 633 nm leads to their death, while HER2-negative cell treated and illuminated identically stay alive. We suggest (see Fig. 2) that the DARPin coating layer is removed from the particles by proteolysis in lysosomes and the uncoated particles aggregate into multiparticle structures that efficiently absorb light at wavelengths longer than 600 nm. The results reported here pave the way to developing photodynamic approaches for specific treatment of cancer.

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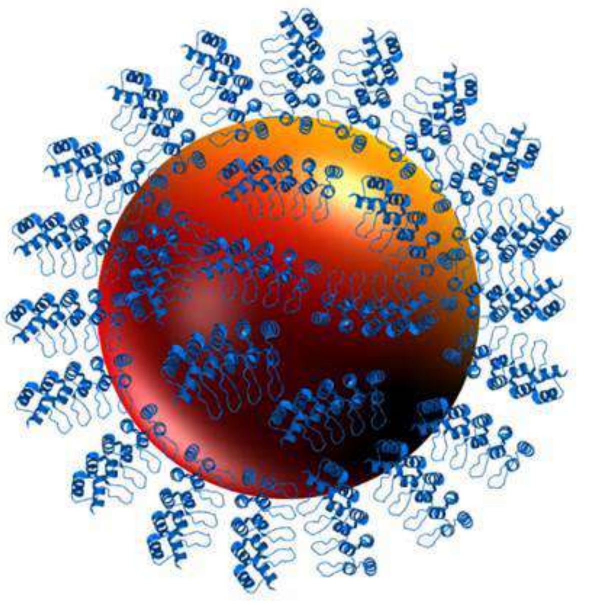

Figure 1: Schematic drawing of a gold nanoparticle (red sphere) DARPin_9-29 (blue spiral-shaped structures) conjugate.

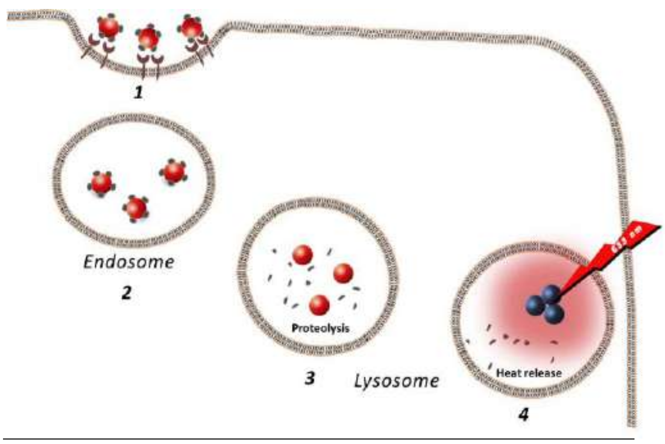

Figure 2: Tentative mechanism of light-induced elimination of HER2-positive SKBR-3 cells. 1 - Binding of DARPin-GNPs through high-affinity interaction of the DARPin molecules on the surface of the conjugate with the receptors on the cell membrane; 2 - internalization of the conjugates by endocytosis; 3 - digestion of the DARPin coating layer by lysosomal proteases; 4 - binding of uncoated nanoparticles and formation of multiparticle structures that can efficiently absorb light at wavelengths above 600 nm. The heat generated upon the illumination severely damages and kills the host cell.

Ultrahigh Frequency Phononics and Mechanics

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Acoustic phonons in the sub-THz range have emerged as a suitable platform to study complex wave physics phenomena. This has spurred the development of a large bandwidth of versatile nanophononic devices for full control and manipulation of phonons on the few-nm length scale. Furthermore, the strong interactions between acoustic phonons and other excitations in solids extend the range of applications for nanophononic devices into other areas of research such as optoelectronics and optomechanics.

The simultaneous engineering of optical and phononic properties led to a new kind of structures called phoXonic crystals capable of confining simultaneously photons and phonons [1]. Usually, in one-dimesional systems an optical microcavity is formed by two identical distributed Bragg reflectors embedding an optical spacer, acting in a similar way to a Fabry-Perot resonator. By the same token, an acoustic nanocavity is usually formed by two distributed Bragg reflectors (DBRs) enclosing an acoustic spacer [1-3]. Layers with thickness of a few nanometers, and atomically flat interfaces are two strong requirements to fabricate devices capable of manipulating acoustic phonons in the GHz-THz range.

Recent advances in material science and fabrication techniques enabled the fabrication of nanometric devices in which photons (VIS-NIR) and phonons (GHz-THz frequencies) are simultaneously confined in a single resonant cavity giving rise to unprecedented large optomechanical coupling factors [1,4-5]. In addition, the engineering of acoustic waves with GHz-THz frequencies is also at the base of the study of mechanical quantum phenomena and non-classical states of mechanical motion.

In this presentation I will first introduce and compare strategies to generate, manipulate and detect ultra-high frequency acoustic phonons using either ultrashort laser pulses or high resolution Raman scattering. Second, I will describe the acoustic behavior of standard nanophononic Fabry-Perot resonators and finally present experimental and theoretical results on a series of novel nanomechanical devices able to control the phonon dynamics at the nanoscale.

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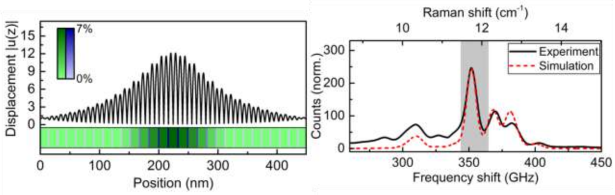

Figure 1: Displacement distribution as a function of position in a phononic adiabatic cavity (left). The thickness deviation from the periodic structure is shown with a color scale. Comparison between the simulated and measured Raman scattering (right). The confined acoustic cavity mode peak is indicated in grey.

Sharpening Plasmon Resonances in Gold Nanorods

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Although seeded-growth methods have made available to us an extensive library of anisotropic metal nanoparticles [1], the chemical complexity of the growth solution, often involving organic additives [2], and the structural instability of the seeds hinder the quest for high quality products. For the sake of synthetic simplicity, merging different synthetic protocols by finding common growth routes, is a mandatory step to reach a universal growth mechanism and reproducible fabrication.[3] This communication will introduce two recent discoveries, related to improving the optical quality of both pentatwinned and single crystal gold nanorods.

We recently demonstrated that a thermal treatment of small seeds results in extensive twinning and a subsequent drastic yield improvement (>85%) in the formation of different types of pentatwinned nanoparticles, including nanorods, with a high monodispersity and tunable aspect ratio [4].

On the other hand, although single crystal Au nanorods can be readily obtained with very high quality directly from optimized seeded growth methods, polydispersities below 10% are still difficult to reach, which leads to some broadening of the longitudinal LSPR band. We show here that irradiation with a femtosecond laser, at selected conditions of fluence and surfactant concentration, may lead to significant narrowing of the LSPR band, even to the limit of the single particle, as calculated from theoretical models, meaning pure "optical monodispersity".

All together, these results represent a paradigm shift in anisotropic gold nanoparticle synthesis.

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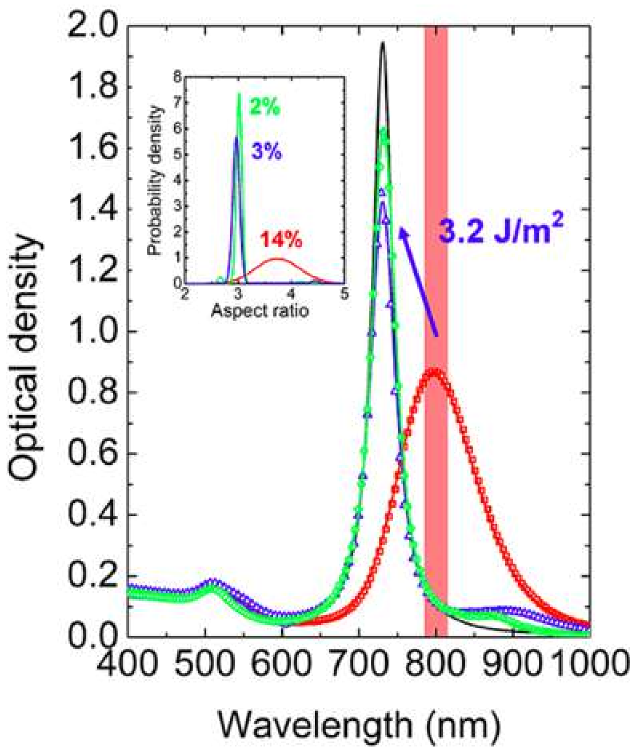

Figure 1: Experimental (symbols) and fitted (lines) optical density spectra of Au nanorod colloids, before (red) and after (blue) irradiation with 800 nm 50-fs laser pulses (represented by the red vertical band) and a fluence of 3.2 J/m2, for 1 h. The normalized spectrum (optical density of 0.15 at 400 nm) of the purified irradiated colloid (green) nearly matches that calculated for a single particle (black). The inset shows the aspect ratio probability densities derived from optical fits.

Halide Perovskites Nanocrystals: Synthesis, Transformations and their Application in Devices

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Halide perovskite semiconductors can merge the highly efficient operational principles of conventional inorganic semiconductors with the low-temperature solution processability of emerging organic and hybrid materials, offering a promising route towards cheaply generating electricity as well as light. Perovskites not only show exceptional primary optoelectronic properties such as a direct bandgap, small exciton binding energy, low carrier recombination rates, ambipolar transport, and tunability of the bandgap covering a wavelength range from the near-infrared to the ultraviolet, but they are also very attractive for their ease of processability for mass production (e.g. printing from solution) and for the large availability of their chemical components. Following a surge of interest in this class of materials, research on halide perovskite nanocrystals as well has gathered momentum in the last three years. In such a narrow time span, several properties/features of halide perovskite nanocrystals were investigated, among them electroluminescence, lasing, anion-exchange, as well as control of size and shape such that nanocrystals in the quantum confinement regime were recently reported. The present talk will highlight the research activities of our group on halide perovskite and perovskite-related nanocrystals and films, with emphasis on synthesis, as well as structural, chemical, and surface transformations, and their applications in various types of devices.[1-3]

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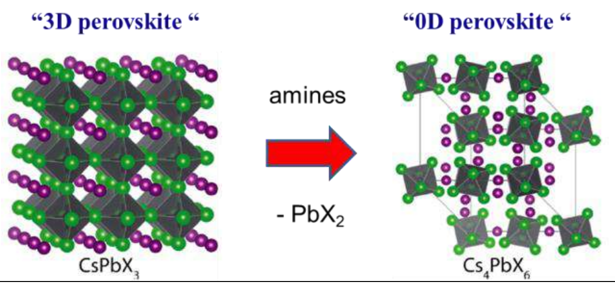

Figure 1: Example of a chemical and structural transformation in nanocrystals of halide perovskites.

Nonlinear dynamics and chaos in Optomechanical nanobeams

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Nonlinear dynamics is a branch of physics that studies systems described by equations more complex than the linear form. Nonlinear systems, such as the weather or neurons, often appear chaotic, unpredictable or counterintuitive, and yet their behaviour is deterministic. In this work we report on the generation and characterization of the nonlinear dynamics of a Si-based optomechanical cavity generated by exploiting nonlinear optical effects typical in silicon resonators and their intercoupling with the mechanical degrees of freedom of the system [1].

For a given wavelength and power in the cavity, the dynamical solution of the system can be a self-sustained oscillation called self-pulsing that modulates light in a coherent way. When a harmonic of the main frequency of the self-pulsing is resonant with a mechanical mode there is a strong amplification of the motion leading to a "phonon lasing" regime (bottom panels of Figure 1)[2] . If the number of photons is large enough, the dynamics of the system became increasingly complex and evolve towards a period-doubling cycle and finally chaos (upper panels of Figure 1). The results of our work could be exploited in many ways but we will discuss their possible implications towards secure communications based on chaos using optomechanical systems.

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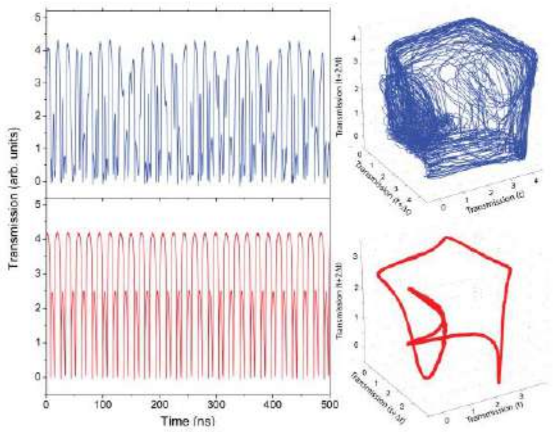

Figure 1: Demonstration of transition between the coherent and chaotic optomechanical regimes. Left: Transmission of the optical signal as a function of time showing a coherent process (lower trace in red) and a chaotic signal (upper trace in blue). Right: Reconstruction of the embedding states in a three-dimensional projection as extracted from the temporal signals of the left panels.

Silicon nitride membranes: jack of all electromechanical trades

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The fields of opto- and electro-mechanics are rapidly growing, with impressive results such as ground state cooling [1,2] already achieved. The full potential of this new fields lays in using mechanical vibrations as a "Universal Serial Bus" for quantum objects, towards the ultimate goal of building hybrid systems for an improved quantum technology. Main challenge to this ambitious goal is to build a platform where two or more quantum systems couple strongly to a common mechanical element without spoiling their own individual characteristics. To this end, silicon nitride offers extraordinary capabilities: it is a low-loss, high index material in the NIR while keeping a low loss tangent in the RF range and it is therefore able to work with metallic superconductors. Further, and even more importantly, Si_3N_4 possesses remarkable mechanical properties, thanks to its tensile stress which allows one to produce structures with incredible aspect ratios. Exploiting these features, I will show how silicon nitiride membranes can be used to host electromechanical superconducting LC resonators based on Al, where ground state cooling of a capacitively coupled, low-frequency flexural mode of a nanobeam has been achieved, as well as field-enhanced strong coupling [3].
Starting from this point, I will present some perspective results to couple silicon nitride membranes to molecular spins through a RF, superconducting (high-T_c) resonator, with the possibility of employing the long mechanical lifetimes as memories for spin-based qubits.
Moreover, I will show how the tensile pre-stress of silicon nitride can be fully exploited not only to realize linear capacitors with small gaps, but even to perform strain engineering on planar materials deposited on top of the membrane, in particular towards the realization of triaxial strain and pseudo-magnetic fields in graphene monolayers.

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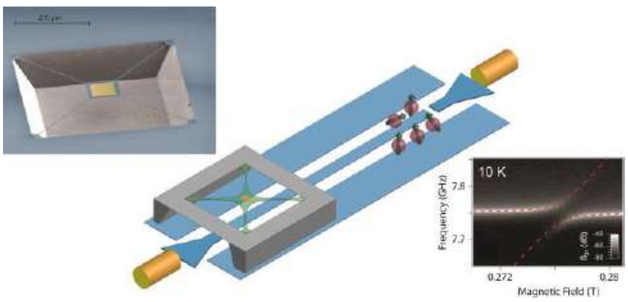

Figure 1: Quantum hybrid system: a silicon nitride trampoline membrane and an ensemble of molecular spins are coupled to the same coplanar waveguide resonator. Spins and photons have already shown strong coupling (colormap in figure) at high-T (from [4]).

Nanoporous Metallic Networks: A New Class of Materials

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Nanoporous metals are artificial and therefore their properties are a direct result of the preparation strategy. Practically, all the current available preparation techniques are multistep, and the resulting nanoporous metal contains foreign additives which eventually govern their optoelectronic properties and may deteriorate their performance. Dealloying, sacrificial templating and colloidal chemistry are the most common strategies use to fabricate nanoporous metals. The inner architecture of nanoporous metals consists of random sizes and shapes of both particles and holes. Consequently, these metallic architectures are able to interact with the entire solar spectrum through excitation of surface plasmons (SPs), a collective oscillation of the metal's free electrons. In a context of photo-catalysis, metallic nanostructures with a characteristic length smaller than 30 nm are important because of the high probability to excite charge carriers upon SPs decay. These excited carriers may be transferred to species in proximity and drive chemical transformations. Therefore, assembly of metallic nanoparticles (NPs) into pure nanoporous three-dimensional (3D) networks is valuable for many applications, while posing a significant challenge.

The resulting networks have distinct colors, different from the corresponding bulks, depending on the type of metal and the network thickness. The large-scale networks are transparent, flexible, pure, and show indication for hot carriers generation and photo-catalytic activity upon white-light illumination.

Those metallic networks bridge the nano world into the macroscopic world and therefore may pave the way for novel materials with unique opto-electronic properties.

I will discuss the method we develop to reach those large scale metallic networks, as well their linear and nonlinear optical properties.

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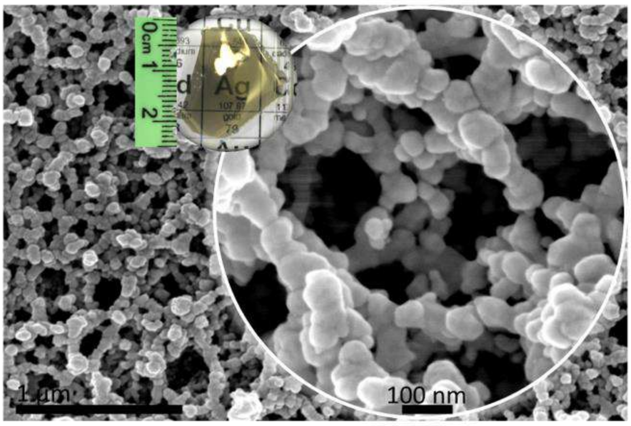

Figure 1: Large-scale nanoporous silver network.

Insights into nanoplasmonics from first-principles time-dependent density functional simulations

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Our optimal implementation of time-dependent density functional theory within linear response allows computing the optical properties of systems with several thousands of atoms [1,2]. We applied this method to study the dependence of the near-field enhancement and localization on the structural details of the plasmonic nano-gaps [3,4], the different size dispersion of the plasmon resonance of silver and sodium nanoparticles and how this behaviour correlates with the presence of 4d electrons in the Ag case [2], and more recently to describe valence EELS [5].

In this talk I will concentrate mostly in the correlation between transport properties across sub-nanometric metallic gaps and the optical response of the system. In Ref. [6] we presented a study of the simultaneous evolution of the structure and the optical response of a plasmonic junction as the particles forming the cavity approach and retract. Atomic reorganizations are responsible for a large hysteresis of the plasmonic response of the system, which shows a jump-to-contact instability during the approach process and the formation of an atom-sized neck across the junction during retraction. Our calculations show that, due to the conductance quantization in metal nanocontacts, small reconfigurations play a crucial role in determining the optical response. We observe abrupt changes in the intensity and spectral position of the plasmon resonances, and find a one-to-one correspondence between these jumps and those of the quantized transport as the neck cross-section diminishes. These results point out to a connection between transport and optics at the atomic scale at the frontier of current optoelectronics.

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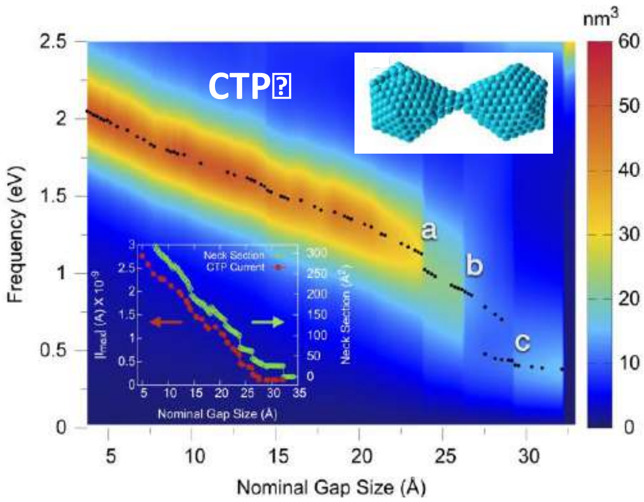

Figure 1: There is a one-to-one correspondence between the jumps in the current flowing through the metal neck, its cross-section and the far-field optical response at the frequency of the so-called charge transfer plasmon (CTP).

The Last Nanometer – Deep Look into the Hydration Structure of DNA and Solid Surfaces Using Ultra-High Resolution AFM

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Abstract

The nature of the interface between biomolecules or solid surfaces with adjacent water molecules governs the interaction of these objects with other molecules or surfaces. Recent advancements in dynamic-mode atomic force microscopy and 3d force spectroscopy open a new window into the study of these short-range phenomena, which are generally inaccessible to other methods. In my talk I will present two recent ultra-high resolution studies of DNA hydration on one hand, and the hydration of hydrophobic surfaces on the other hand. In the first case I'll show that labile water, namely water participating in biological reactions, are concentrated mostly along the DNA grooves and less so on the phosphate backbone. In the second case I'll show that hydrophobic surfaces are coated with a thin layer of gas molecules that renders them certain universality, regardless of the underlying surface. This picture will be used to identify the origin of hydrophobic interaction – a long standing puzzle of physical chemistry.

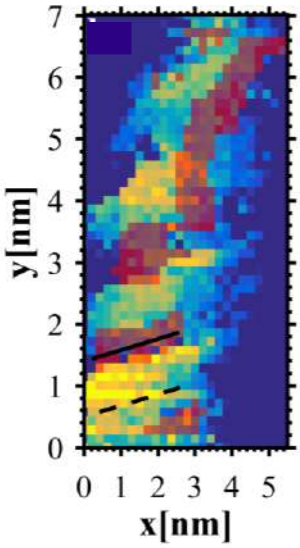

Figure 1: DNA hydration map

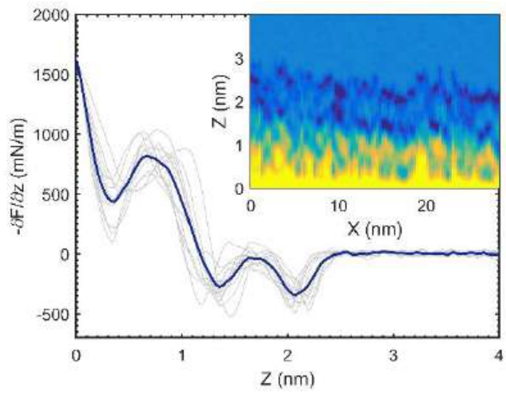

Figure 2: Gas molecules accumulation near hydrophobic FDTS monolayer

Phonon-mediated Nanoscale Thermal Transport

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Phonons play an important role in thermal energy transport in non-metallic solids and in liquids and their study is motivated especially by the need to understand and control thermal transport in the nanoscale [1]. While there are several theoretical approaches, the experimental research has only recently taken off significantly after a slow start. The main reasons have been sample preparation in a controlled manner [2] and the emergence of novel experimental methods [3]. In this talk we will provide an overview and examples of thermal transport in several sample types to illustrate this dynamic and exciting field. The impact of this research encompasses the science of lattice vibrations at interfaces and thin films, coupled state variables as in opto-mechanics, as well as applications in, e.g., thermal interface materials, thermoelectricity and acousto-metamaterials, among others. From Si [3] and MoS_2 [4] membranes to 2D phononic crystals [5] and III-V semiconductor structures [6] we will illustrate key concepts and research issues, such as how the volume-to-surface ratio [7], phononic crystal periodicity, disorder [8] and air convection [7] impact on thermal phonon propagation. We will also discuss perspectives for future research.

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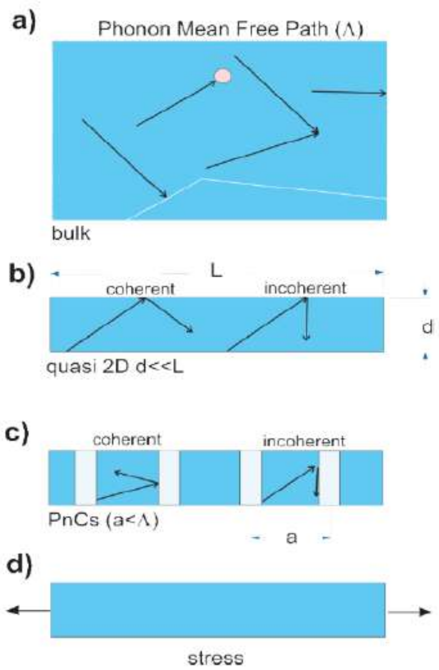

Figure 1: Phonon engineering. Schematics of thermal phonon transport in a bulk (a), a membrane (b) and a 2D phononic crystal (c). Phonons can also be modified by applying stress thereby modifying their dispersion relations (d).

Exciton-phonon interaction in coupled quantum wells: optical refrigeration and optomechanics

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Abstract

Coupled quantum wells (CQWs) confine electrons and holes in spatially indirect regions as shown in Fig. 1, leading to very long radiative lifetimes on the order of 100 ns. We show that this gives sufficient time for relaxation by phonon emission to the excitonic ground state through the excition Mott transition [1]. Since the higher-lying states in the CQW are spatially direct and thus have a much shorter lifetime, CQWs constitute a novel and promising platform for optical refrigeration with cooling efficiencies beyond that of single quantum wells. Finally, we show that the long lifetimes allow matching the timescale of deformation-potential-driven optomechanical interactions to the period of the mechanical resonances, leading to very strong optomechanical forces using free-free membranes as shown in Fig. 2. We find that the carrier-mediated optomechanical forces are 500-fold stronger than radiation pressure [3].

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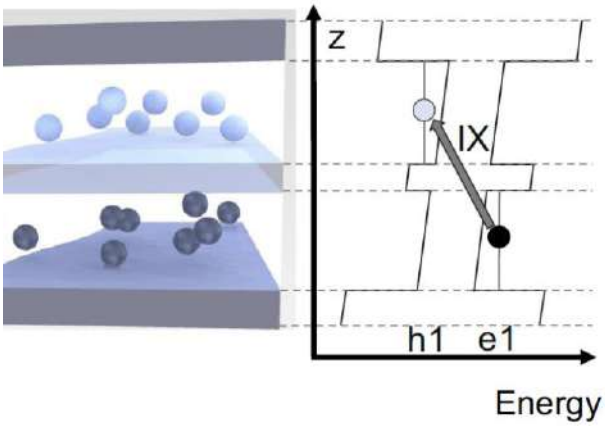

Figure 1: Coupled quantum wells confine electrons (dark blue) and holes (light blue) and the lowest-energy transition connect electrons (e1) and holes (h1) are spatially separated, leading to very long lifetimes [1].

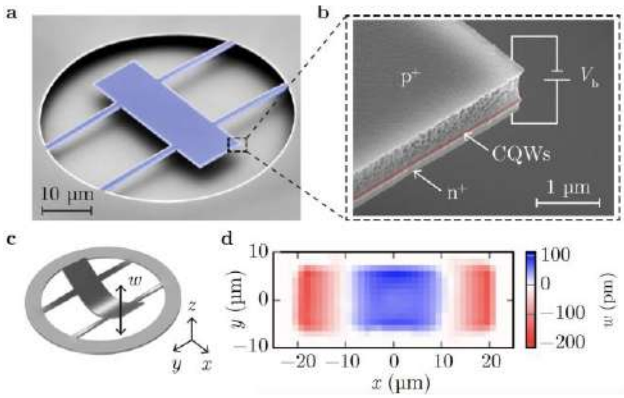

Figure 2: Free-free optomechanical membrane with embedded coupled quantum wells. **a**: Scanning electron micrograph, **b**: Zoom-in showing the doped contact layers, **c**: Simulation and **d**: Measurement of the fundamental mechanical mode of the membrane with the color scale showing the deformation [3].

Nonlinear and pulsed optomechanical measurement in sliced photonic crystal nanobeams

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In optomechanical systems, co-localizing light and mechanical oscillations at the nanoscale can lead to strong interaction between photons and phonons. Such optomechanical coupling enables extremely sensitive detection of nanoscale motion, that allow exploring the fundamentals of quantum measurement as well as novel sensing technologies. Linear continuous measurements of mechanical resonator position are famously limited by Heisenberg's uncertainty principle, in the form of the Standard Quantum Limit (SQL). We study optomechanical systems in which photons and phonons are coupled with extreme strength, to demonstrate new applications of nonlinear and non-continuous measurement of nanomechanical motion.
We study 'sliced' photonic crystal nanobeams (Fig. 1), which host optical cavity modes that are confined to a 40 nm gap, thereby establishing record photon-phonon coupling rate of 25 MHz to the flexural mechanical modes of the nanobeam. Over a wide range of temperatures, the natural thermomechanically-induced cavity frequency fluctuations dominate the apparent optical linewidth (Fig. 2). The system thereby operates in a new nonlinear regime, which pronouncedly impacts optical response, displacement measurement, and radiation pressure effects [1]. We demonstrate that the strong nonlinearity can be used to perform sensitive quadratic position measurement – a promising route towards the creation of phonon number states of the mechanical resonator [2]. Moreover, we show that the instantaneous resonator position can be resolved with single nanosecond pulses, approaching the regime where they could surpass the standard quantum limit of continuous measurement [3].

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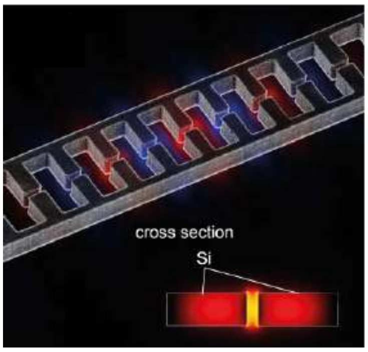

Figure 1: Sliced photonic crystal nanobeam

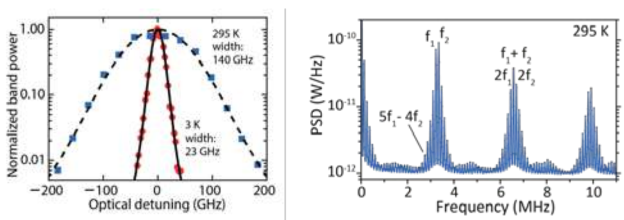

Figure 2: Nonlinear optomechanics with thermal fluctuations: (left) Effective optical linewidth dominated by thermomechanical fluctuations. (right) Nonlinear measurement of mechanical motion.

3PM2018 – ORALS

Anderson co-localization in GaAs/AlAs superlattices

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Engineered cavities in optomechanical crystals exhibit Q-factor degradation and optomechanical coupling rate reduction due to extra-loss mechanisms and mode hybridization induced by intrinsic fabrication disorder. An alternative to further intensify efforts on improving nanofabrication techniques is to use disorder as a tool to localize light and mechanical motion by using Anderson localization. Numerical simulations of position-disordered silicon nanobeams [1] show that the average optomechanical coupling achievable is rather moderate due to low probability of co-localized photon-phonon pairs. In order to guarantee a high degree of spatial co-localization, GaAs/AlAs superlattices seem to provide the ideal platform. Longitudinal motion and light propagation in the epitaxy direction obey the exact same equations due to a somehow magical coincidence in velocities and impedances [2], therefore guaranteeing *perfect* co-localization. We assess Anderson localization of both photons and phonons in such system by using a standard transfer matrix approach and discuss the role of spatial co-localization for cavity optomechanics experiments by comparing it to other typically used superlattices (Si/Ge, $BaTiO_3/SrTiO_3$).

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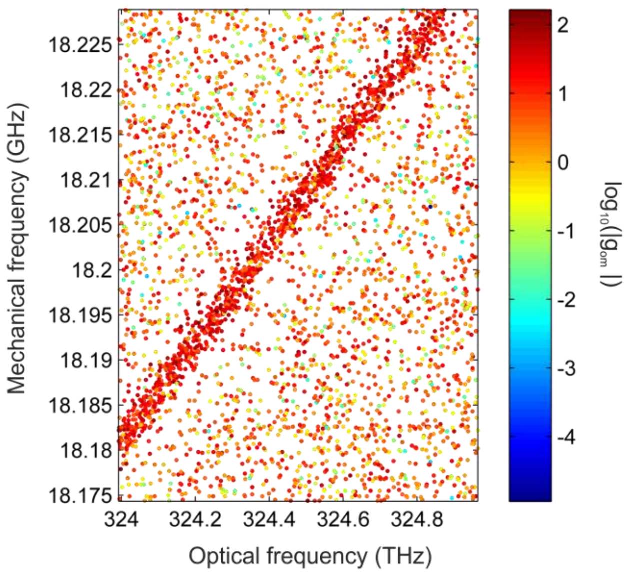

Figure 1: Vacuum optomechanical coupling rate g_{om} realizations for disordered ($\lambda/2$, $\lambda/2$) - GaAs/AlAs superlattices. The pronounced diagonal is the fingerprint of Anderson co-localization.

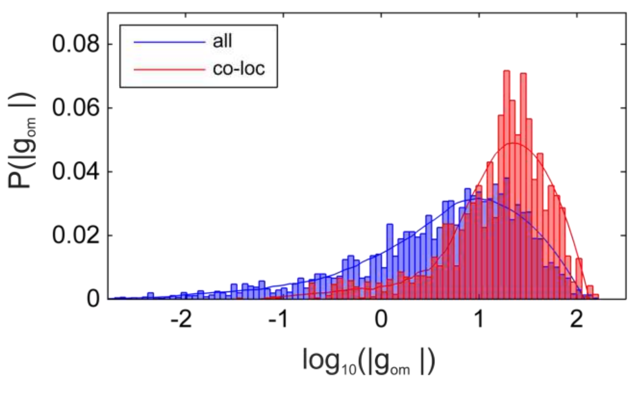

Figure 2: Probability density function of the vacuum optomechanical coupling rate g_{om} for all photon-phonon pairs (blue) and considering only co-localized pairs (red).

Tunable Fano Resonances in Colloidal Photonic Structures

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Asymmetric resonances can occur in many different experiments belonging to different fields and the way we describe them is by using a special shape U. Fano found in 1935 analysing the Rydberg absorption lines in noble gases [1]. These line-shapes are the result of two interacting resonances and the final asymmetry depends on the strength of that interaction. In photonics, they often appear in many systems like plasmons, photonic crystals or meta-surfaces, to name just a few. In this field, Important applications such as sensors, switchers or lasers are envisioned where, taking advantage of Fano line-shapes, their performance can be controlled and enhanced [2]. However, in many situations identifying the different interacting resonances is not trivial and thus, the desirable control of their interaction turns impossible.
In this talk, I will give some examples, all of them performed in colloidal photonic crystals, where such interaction can be tuned by different means. I particular, I will discuss how by controlling the number of vacancies present in a self-assembled photonic crystal one can finely tuned disorder and through it, the optical response of the system. This response can be easily correlated using the Fano formula to the interaction between band gap and the continuous provided by Mie Scattering. Further and interestingly, Fano parameter q vanishes when the system crosses the percolation threshold for vacancies [3].

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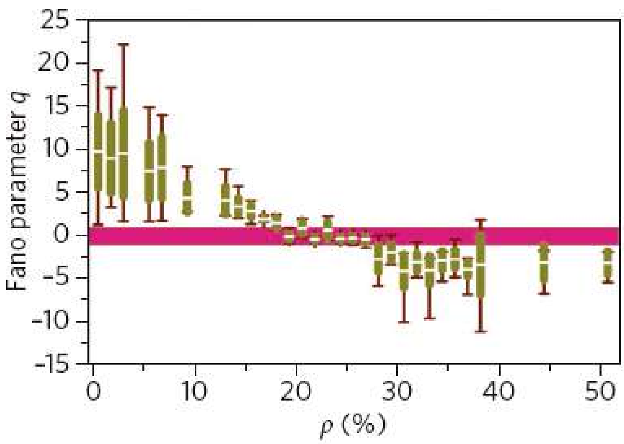

Figure 1: Fano parameter q as a function of the density of vacancies randomly included in a colloidal photonic crystal.

In-flow and in-continuum refractive index sensing using a highly sensitive porous silicon ring resonator

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Traditional planar photonic sensing structures based on a high index contrast configuration present a limitation affecting their sensitivity: only the evanescent field propagating outside the photonic structure is used for sensing purposes, while the majority of the optical field is confined within the structure itself. To overcome such limitation, we developed a highly sensitive photonic sensor based on a porous silicon ring resonator (PSRR). The porous silicon platform allows the infiltration of the target substance directly into the pores in order to obtain an increased sensitivity [1,2]. The photonic sensing structure was fabricated by using a high index contrast nanoporous silicon platform, consisting of a porous silicon double layer. A low porosity top layer was used to form the PSRR by e-beam lithography, whereas a high porosity bottom layer was used to confine light in the vertical direction (Fig. 1). The sensing performance of the PSRR was characterized by means of several refractive index sensing experiment. An opto-fluidic setup was developed to flow several solutions with different refractive indices over the photonic sensor and, at the same time, to monitor in-continuum the evolution of the PSRR spectrum (Fig. 2). PSRR presented a sensitivity of up to 439 nm/RIU (Refractive Index Unit). The average value of the noise observed in the experiments was 0.1 pm, leading to a limit of detection of only $2.2 \cdot 10^{-7}$ RIU.

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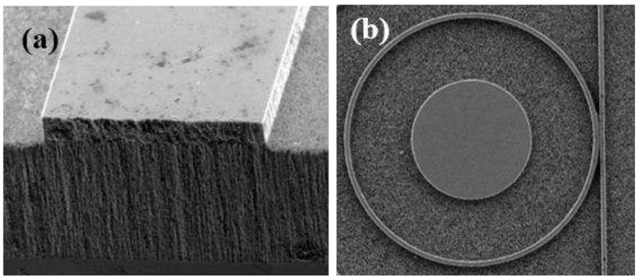

Figure 1: (a) 60°-sectional FE-SEM image of the 10µm-wide access waveguide. (b) Top-view image of the RR and the coupling waveguide.

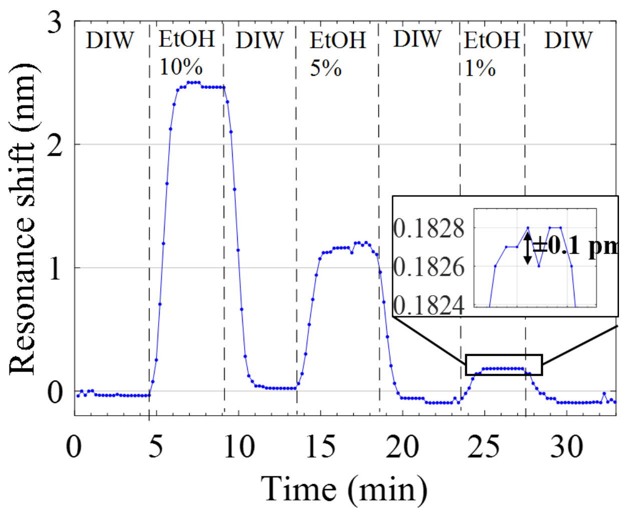

Figure 2: PSRR resonance wavelength shift time evolution.

Magnon detection on high Q-microspheres

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The possibility of controlling spin waves with electromagnetic radiation in the development of future quantum communications is called to play a central role. In particular, the use of collective excitations in magnetically ordered materials, i.e., magnons, are considered very useful because of their high tunability (from MHz to THz).

In this work we demonstrate the local detection of magnon modes pumped resonantly in a YIG film. We optically excite a high quality factor ($Q=10^5$) whispering gallery modes of a nonmagnetic microsphere, whose evanescent tail interacts with the magnon mode. The transduction principle explored in this experiment is very similar to the mechanism used in optomechanics [1]. We compare our results with those obtained in YIG spheres that display high-Q optical modes [2]. Indeed, since a spherical magnon cavity is no longer required, these results may enable developing an on-chip opto-magnon technology.

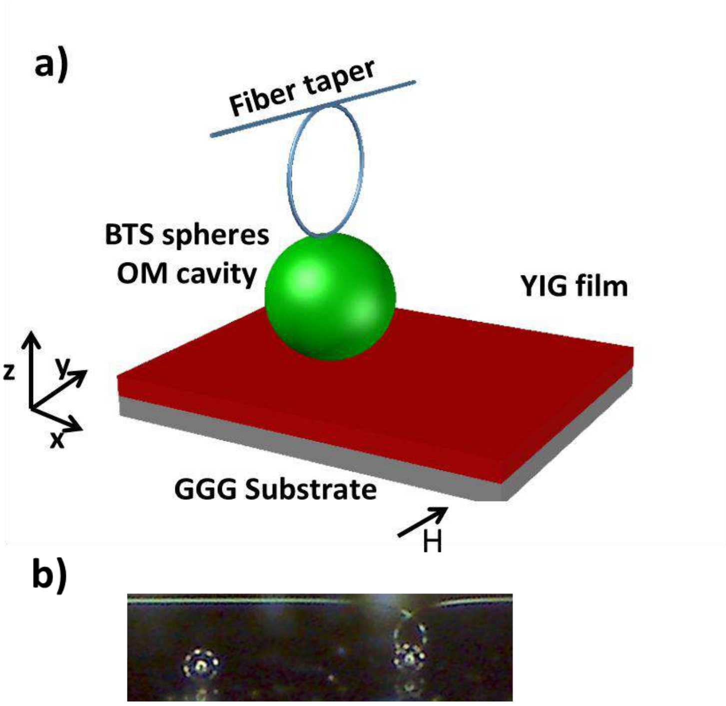

Figure 1: (a) Schematic illustration of the experiment. Magnons are localized on a ~100nm YIG film grown over a GGG substrate. We employ BTS spheres with diameters around ~50µm as an optical cavity with high quality factors ($Q>10^5$). The light is coupled evanescently to the sphere with a tapered fiber connected to the laser source. (b) Lateral view of the BTS spheres and the tapered fiber.

*Equal supervision

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Cellulose based photonic architectures

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Cellulose is the most abundant polymer on Earth and for centuries has had a wide technological impact in areas such as textile, packaging or knowledge storage. It is biodegradable, biocompatible and possesses excellent mechanical characteristics that have raised the interest of many engineering fields [1]. The versatility of cellulose has opened new venues in advanced materials in electronics, energy or biological applications [2]. Here we introduce a cellulose derivative as an eco-friendly and water developable resist. We combine cellulose with nanoimprinting lithography (NIL), the most promising method for mass-produced inexpensive nanostructures over large areas and with a very low density of defects [3]. Using cellulose as a resist and NIL, we are able to pattern silicon wafers or fabricate metallic nanoparticle arrays using water as the only solvent. Furthermore, we revolutionize the field of transient photonics by directly moulding the cellulose itself into photonic and plasmonic architectures and illustrate their outstanding performance in several applications such as structural colours, photoluminescence enhancement and as disposable Surface Enhanced Raman Scattering substrates.

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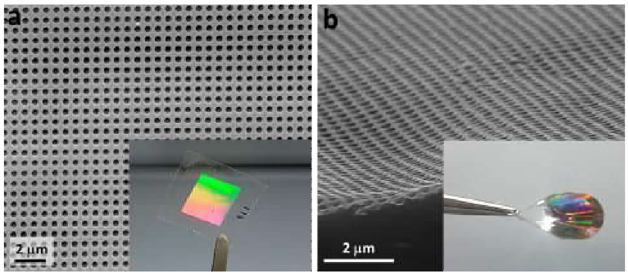

Figure 1: SEM of Cellulose based Photonic (a) and Plasmonic (b) crystals. A photograph of each sample is included as an inset for each case; patterned areas are 1x1 cm2

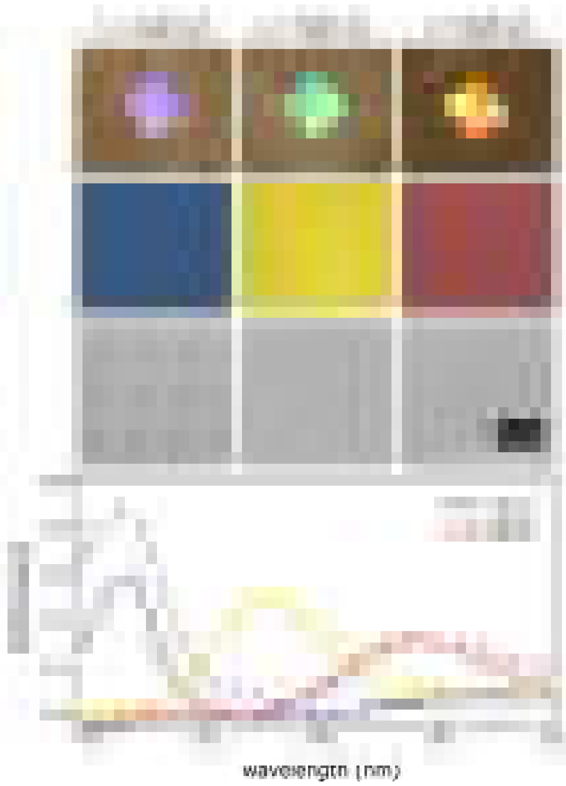

Figure 2: HPC photonic crystals present iridescent colours that depend on the lattice parameter of the nanoimprinted structure.

Photonic applications of nanocolumnar Au films obtained by glancing angle deposition with magnetron sputtering

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In the last few years, we have fabricated metallic coatings with nanocolumnar morphology by means of glancing angle deposition with sputtering [1-3]. This technique allows for obtaining nanostructured coatings onto any kind of flat substrates and it can be scaled up to large areas. Depending on the deposition parameters (such as gas pressure, tilt angle, substrate rotation, etc.), the nanocolumnar structure can be controlled, giving rise to different properties [4]. In particular, for gold coatings we have obtained specific optical properties related to the existence of localized surface plasmons associated with the nanopillars.

When vertical nanocolumns are produced by using substrate rotation and high tilt angle, the coatings show black metal behaviour in the visible range [5], with reflectivity below 10% in the 400-700 nm range (see Figure).

On the other hand, when short tilted nanocolumns are fabricated, hot spots of electromagnetic field develop and provide a strong enhancement of the fluorescence or Raman signals. As a result, this is a low cost approach to prepare SERS substrates by a physical vapour deposition technique.

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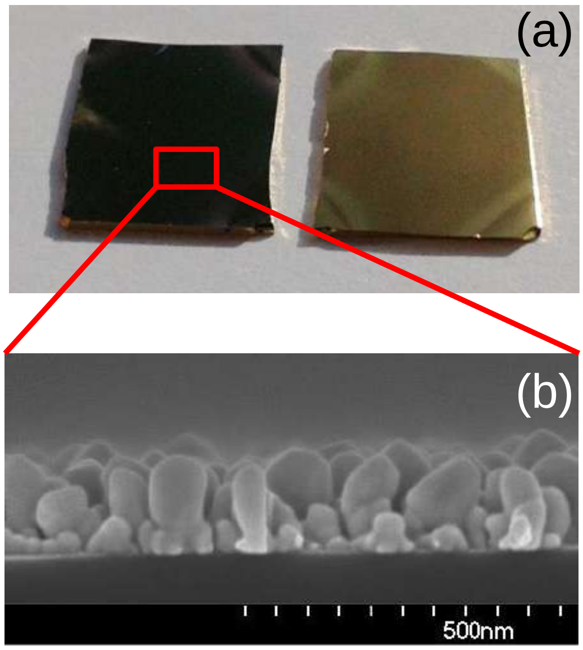

Figure: (a) Photograph of two Au samples prepared by glancing angle deposition with sputtering onto rotating Si substrates with deposition angles 87° (left) and 75° (right). Notice the black colour of the left sample. (b) Cross section SEM image of the left sample.

SPIN PLASMONS AT SURFACES WITH STRONG SPIN-ORBIT COUPLING

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Understanding the role of the spin in the dynamics of many-electron systems has become a topic of major interest during the last few years, with the advent of several fascinating phenomena such as the Spin-Hall effect, the Edelstein effect, or the recently discovered topological phases of matter [1]. All these effects rest on the profound connection that the relativistic spin-orbit coupling imposes between the electronic charge and spin degrees of freedom.

More specifically, surfaces and interfaces with strong relativistic effects show a sizeable spin-splitting of its electronic surface states, leading to complex and well-defined spin textures even in nominally non-magnetic systems [2].

In this oral communication, I will present the impact that spin-orbit coupling may cause on the plasmonic properties of such surfaces. For that purpose, we generalize the linear response formalism in order to include the full spinor nature of the electronic wave functions, and perform first-principles calculations within the TDDFT framework. We show, using the Tl/Si(111) surface as an example, that the spin-texture of the conduction electrons give rise to a novel coupled spin-charge plasmon mode, which is composed of a strong spin-density oscillation together with the usual charge-density oscillation, and which is localized at the first few atomic layers of the system [3].

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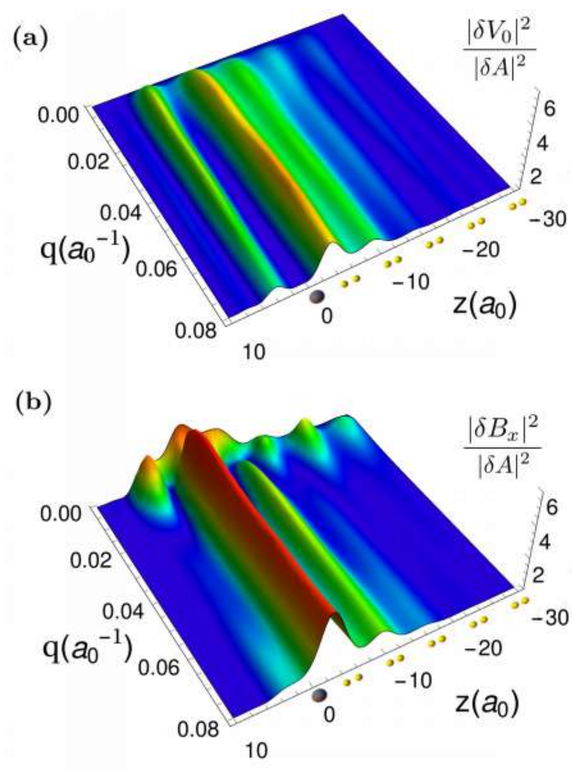

Figure 1: Real-space structure and momentum (q) dependence of the coupled spin-charge plasmon. The normalized charge and transversal-spin components of the self-sustained oscillation are shown with respect to the z coordinate, the direction perpendicular to the surface. Negative values of z correspond to penetration into the bulk, and orientative positions of the first thallium and silicon atomic layers are represented by big gray and small yellow spheres, respectively.

Photosynthetic photonic crystals: photonic aspects of the ultimate light harvesting process in nature

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From a molecular point of view photosynthesis (PS) is the ultimate light harvesting process in nature showing efficiencies not yet achievable with any synthetic chemistry approach [1]. However, one side of PS that has been seldom explored is the effect of complex photonic environments over the photochemistry of PS.
With this paper we aim to give a flavour of the potential that photosynthetic photonic systems represent for biomimetic light harvesting technologies. To illustrate this potential we will show two examples of natural photonic structures in plants and algae with different yet important roles in light management and PS.
As a first example we will discuss the presence of organelles formed by multilayers of photosynthetic tissue present in the cells of some species of the genus *Begonia* [2]. The tissue is arranged like a Bragg reflector to form a 1D photonic crystal responsible for the strong blue colour of the leaves. Interestingly our work shows that the presence of the photonic crystals can enhance the light harvesting process of the cells at wavelengths suitable for PS.

The second type of natural photonic structure we will discuss is a natural 3D photonic crystal present in the epidermal cells of the alga *Cystoseira tamariscifolia* [3]. These photonic structures are formed by ≈200 nm lipid spheres arranged in an opal-like conformation and contained in intracellular 5-10 µm diameter vesicles located next to the photosynthesis regions of the cells. We will show that these natural photonic crystals are responsible for the strong structural colour shown by this alga. More interestingly we will also demonstrate that the photonic response is dynamic. Morphological changes in the arrangement of the spheres are triggered by changes in the light environment. The nanospheres arrange in an ordered (randomized) conformation under dark (light) conditions suggesting a mechanism to tailor light propagation within the cells.

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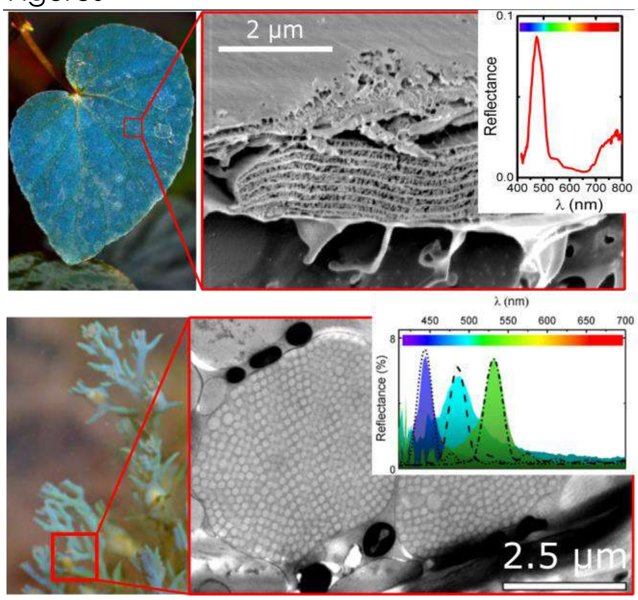

Figure 1: Specimen, micrograph and reflectance of natural photonic crystals in *Begonnia pavonina* leaf (top) and algae *Cystoseira tamariscifolia* (bottom).

Nanocrystalline silicon optomechanical cavities

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Cavity optomechanics and opto-mechanical circuits in general have gained popularity and are now used as a versatile framework in which to observe various classical and quantum phenomena involving both light and mechanical vibrations. Many studies focus on non-linear applications due to potentially huge impact of features such as phonon lasing, chaos and high sensitivity readout. Ultra-high quality factor optomechanical cavities have be created with a large number of shapes, such has micro-toroids, spheres, high-finesse Fabry-Perot cavities. Recently, cavities created in planar semiconductor films from specifically engineered one or two-dimensional periodic patterns gained popularity. Similarly, a large number of crystalline and polycrystalline materials were used to create these structures, such as silicon nitride (Si3N4), gallium arsenide (GaAs), aluminium nitride (AlN), diamond, and, of particular importance, crystalline silicon (Si) [1]. Si, in particular via the Silicon-on-Insulator platform that is already widely used in photonics, is especially promising for on-chip applications, due to both its low loss at telecom wavelength and CMOS compatible fabrication process. So far, the focus has been put on high quality crystalline silicon. However, the role of crystallinity is not as straightforward for non-linear applications as for linear ones. Furthermore, crystalline silicon presents two main drawbacks, namely the relatively high cost of the wafers and the limitation to a single thin layer of crystalline silicon.

To remedy to these issues, we have investigated the use of nanocrystalline silicon to create optomechanical devices. We demonstrate that this platform can be used to fabricate optomechanical cavities that display similar features to the crystalline platform, namely optical and mechanical properties that enable thermos-optic/free-carrier dispersion self-pulsing, phonon lasing [2] and chaos [3]. All of these effects occur at low input laser power and we even observed an extremely large tuning of the optical resonance, going as far as 30 nm, which occur due to the lower thermal dissipation rate in this material. Moreover, the self-pulsing induced phonon lasing appear at frequencies as high as 0.3 GHz, which is a factor of 5 higher than its crystalline silicon counterpart. We attribute this improvement to the shorter free carrier relaxation lifetimes.

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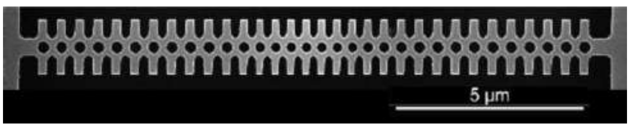

Figure 1: SEM image of the nanocrystalline silicon optomechanical cavity.

Development and experimental study of a porous silicon fiber-optic temperature sensing probe

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Fiber-optic sensors (FOSs) are largely employed in temperature sensing [1], since temperature is a crucial parameter in several fields, especially research laboratories, food industries, environmental monitoring, monitoring of biochemical reactions and military and aerospace uses [2]. However, the majority of fiber-optic temperature sensors make use of the fiber itself as sensing element. This leads to two main limitations: first, the photonic structures are created in the fiber, leading to a more difficult fabrication process; second, the optical fiber is made of silica, which is characterized by a relatively low thermo-optic coefficient (TOC), which determines a low sensitivity. To overcome such limitations, we developed a temperature sensing probe created as a result of the combination of an optical fiber and a porous silicon microcavity (PSMC). Several simulations were carried out in order to obtain the physical parameters to achieve the required sensing structure, which was fabricated by electrochemically etching a silicon wafer to create the required porous silicon multi-layer structure. A 1 mm^2 PSMC piece was attached to the tip of an optical fiber, so that temperature variations can be monitored exactly on that point and in real-time employing an opto-thermal setup (Fig. 1). The performance of the PSMC sensor probe was characterized in a stable system, which was water environment (Fig. 2(a)). A sensitivity around 110 pm/°C was obtained. The average value of the noise observed in the measurements was 0.3 pm. After a filtering process to remove the high frequency components, the noise value was reduced by one order of magnitude, leading to a temperature change resolution in the 10^{-4} °C. Afterwards, the temperature transmission dynamics in air environment was studied (Fig. 2(a)). A less steady signal and a higher level of noise were observed.

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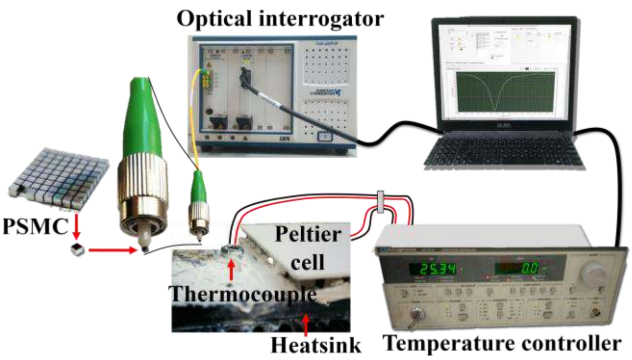

Figure 1: Opto-thermal setup with the PSCM FOS used for the real-time temperature monitoring.

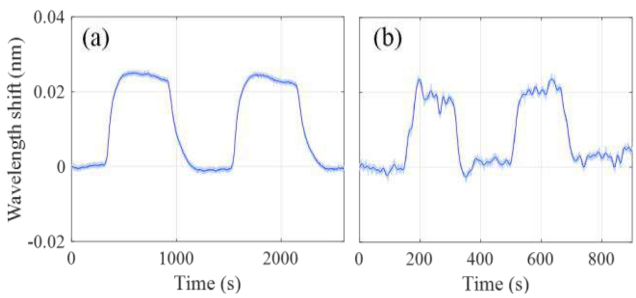

Figure 2: PSMC peak wavelength shift time evolution in (a) water and (b)air.

Gold Nanoparticle-based supercrystals as Surface Enhanced Raman Scattering (SERS) substrates

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We present a straightforward method to produce large area plasmonic crystals with sub-micrometer periodicity using pre-patterned soft molds.[1],[3] We demonstrate the assembly of gold nanoparticles into square lattices with pitch sizes as low as 400 nm. Optical characterization of the supercrystals by means of microspectroscopy allows the identification of distinct extinction peaks that can be attributed to the hybridization of the nanoparticles plasmon resonance with the modes arising from the cluster organization and lattice modes.[2] Further, we show the tunability of the lattice mode resonance throughout the visible and into the near infrared range. Consequently, our supercrystals can be designed to act as surface enhanced Raman spectroscopy substrates that are specifically tailored for a desired excitation wavelength.[4] The SERS response of 4-acetoamidothiophenol has been studied on different supercrystal assemblies and the optimum substrate for 785 nm excitation has been identified. We successfully fabricated large area assemblies of gold nanoparticles acting as SERS substrates, exhibiting exciting optical properties from the visible to the NIR range. These results open up the way to further exploit supercrystal assemblies for sensing and many other photonic applications.

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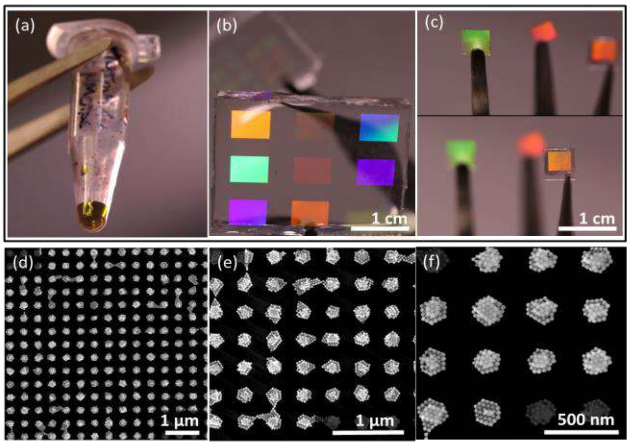

Figure 1: Photograph of (a) colloidal solution of AuNP, (b) PDMS (c) Macro image of NPs assembly (d), (e), (f) top view SEM micrographs illustrating the square lattice of Au NP clusters with different magnifications.

Ultrathin Semiconductor Superabsorbers from the Visible to the Near Infrared

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The design of ultrathin semiconducting materials that achieve broadband absorption is a long-sought-after goal of crucial importance for optoelectronic applications [1]. To date, attempts to tackle this problem consisted either on the use of strong -- but narrowband – or broader --but moderate -- light trapping mechanisms. In this work, we present a strategy that achieves broadband optimal absorption in arbitrarily thin semiconductor materials for all energies above their bandgap. This stems from the strong interplay between Brewster modes [2], sustained by judiciously nanostructured thin semiconductors on metal films, and photonic crystal modes. We demonstrate broadband near-unity absorption in Ge ultrathin films that extend from the visible to the Ge bandgap in the near infrared and robust against angle of incidence variation [3]. Our strategy follows an easy and scalable fabrication route enabled by soft nanoimprinting lithography [4], a technique that allows seamless integration in many optoelectronic fabrication procedures.

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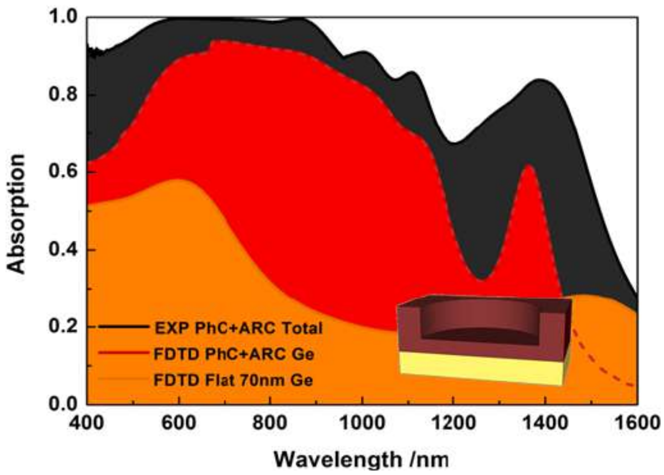

Figure 1: Total absorption of the Nanostructured 70 nm dielectric superabsorber (Black) and absorption in the Germanium (Red) vs the absorption of a flat film of germanium over gold with the same thickness (70 nm) (Orange). Inset: Cross section scheme of the photonic structure.

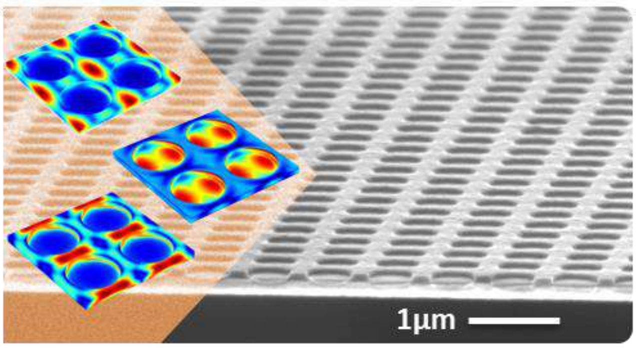

Figure 2: SEM Tilted cross-section image of the photonic architecture and the electric field concentration for its maximum absorption peaks.

Nanophononic Potentials Based on Band Engineering

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Acoustic phonons in the GHz-THz range appear as a suitable platform to study complex wave phenomena, motivating the development of nanophononic devices[1]. The strong interactions with other excitations in solids extend the range of applications to other fields such as electronics and optomechanics[2,3]. In this work we propose a new kind of resonator based on the engineering of the phononic band structures associated to periodic superlattices that allows us to mimic arbitrary electronic potentials.
By modulating the thickness ratio of the two materials forming a one-dimensional periodic superlattice we can adiabatically close and reopen a minigap along the structure. The edges of this engineered bandgap generate the equivalent of a potential well. We can control the energy and the number of bounded nanophononic modes (see Fig. 1). This spatial modulation of the effective band structure allows us to control the symmetries of the edge modes, enabling the implementation of a phononic topological transition that changes not only the energy of the confined modes but also their number and nature.
Acoustic nanocavities[4,5] as the ones showed in this work present confined states similar to the confined electronic levels in atoms and quantum wells. Following this idea, by modulating a minigap following a parabolic curve, one can design a device that confines states in an analogous way of a quantum harmonic oscillator. Such a device is described and the role of different parameters is studied.
The proposed structures can be grown by actual molecular beam epitaxy technology, and experimentally studied through standard coherent phonon generation techniques.

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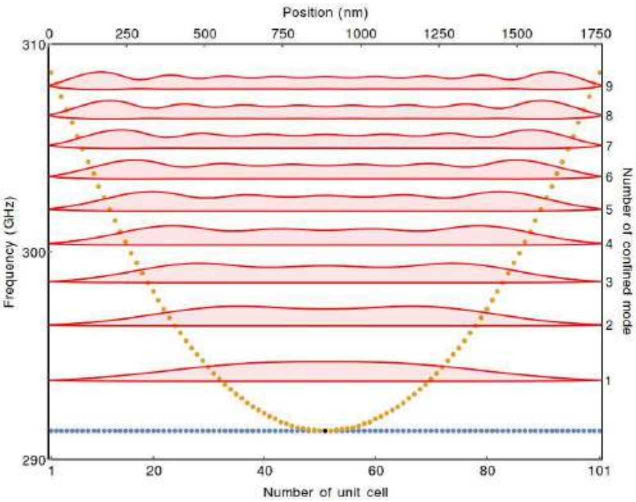

Figure 1: Spatial profile of the displacement amplitude for each confined mode plotted on top of the acoustic band structure with its symmetries encoded in color.

Low-loss bulk and edge plasmons in graphene heterostructures – a theoretical study

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Abstract

Terahertz (THz) fields are widely applied for sensing, communication and quality control. In future applications, they could be efficiently confined, enhanced and manipulated through the excitation of graphene plasmons. Graphene plasmons possess ultra-strong field confinement, enabling new classes of devices for deep subwavelength metamaterials, single-photon nonlinearities, extraordinarily strong light-matter interactions and nano-optoelectronic switches.
We theoretically investigate the properties of graphene plasmons in the bulk and at the edge. For bulk modes, we find that at room temperature the scattering against graphene's acoustic phonons is the dominant limiting factor for hBN/G/hBN stacks. At the edge, the presence of strain fields induces novel charged counter-propagating acoustic edge modes. In the limit of large pseudomagnetic fields, each of them involves oscillations of only one of the two electronic components.
Furthermore, we show that new chiral valley-polarized second-sound collective modes can propagate along the edges of novel materials with non-trivial Berry curvatures.

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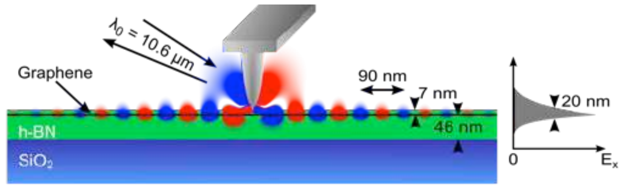

Figure 1: SNOM excitation of graphene plasmons and their lateral field confinement

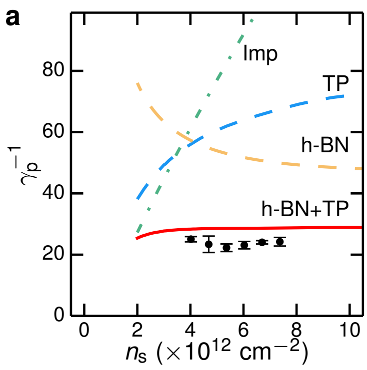

Figure 2: A comparison between experimental and theoretical damping ratios

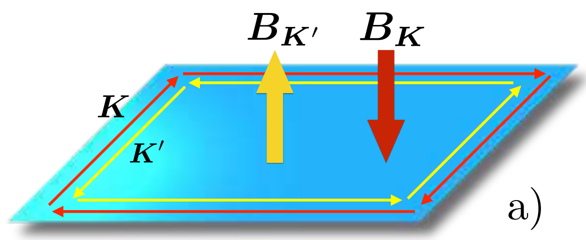

Figure 3: Edge pseudo-magnetoplasmons in the presence of strain fields.

Incorporation of plasmonic nanoparticles in organic photovoltaic solar cells

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Organic photovoltaic (OPV) cells have long-term stability, light weight, and can be fabricated at room temperature. These advantages make them a promising clean and sustainable source of energy and exciting research area. A major challenge in the development of better OPV is the trade-off between light absorption and photogenerated exciton collection, requiring that the polymer film has both high absorbance and low thickness. One promising approach to enhance light harvesting in OPVs is based on the use of plasmonic nanostructures such as gold or silver nanoparticles, which can act as local field enhancers [1,2] and/or light scattering centers [3].

Here, we prepared and characterized gold nanospheres and nanostars and coated them with insulating silica shell of 8 nm to 22 nm to avoid charge recombination (Figure 1). The nanoparticles were incorporated in the active layer containing optically active polymer and acceptor molecules, in order to study the interfacial charge and energy transfer processes at the nanoscale.

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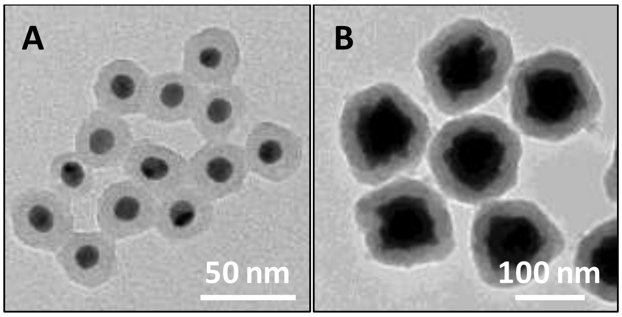

Figure 1: Hybrid core-shell nanoparticles with gold spheres (A) and gold stars (B) in the core encapsulated with a silica shell of 8 nm and 22 nm of thickness, respectively.

Photonic Bandgap Biosensing Structures Biofunctionalized with Molecular Beacon Probes

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Given the relevance of the detection of RNA/DNA for bioanalysis and biomedical research [1,2], we propose a ground-breaking label-free strategy for detecting oligonucleotide strands based on silicon photonic bandgap (PBG) structures biofunctionalized with molecular beacon (MB) probes [3]. Complementary target oligonucleotides were specifically recognized through hybridization with the MB probes on the surface of the PBG sensing structures, exhibiting remarkable PBG edge shifts even in the range of ~1100 pm vs. around 20-90 pm for typical shifts obtained using ring resonator based sensors [4]. These shifts indicate a very high sensitivity of the PBG sensing structure towards small local refractive index variations being produced in its surface. Such high sensitivity was then used to exploit the hairpin conformational changes of MBs upon hybridization for changing the interaction of a particle-labelled MB over a PBG sensing structure, since the conformational change promotes the displacement of the particle away from the surface of the sensor. To this end, a biotin moiety was added to the MB in order to selectively bind a streptavidin molecule to it. Our experimental study demonstrates, for the first time to our knowledge, the influence of the conformational change suffered by MB probes upon the biorecognition of target oligonucleotides over evanescent wave photonic sensors.

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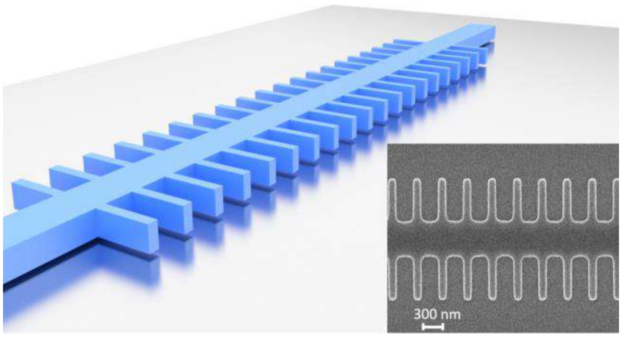

Figure 1: Schematic representation of the 1D PBG sensing structure (inset: SEM image of a fabricated PBG sensing structure).

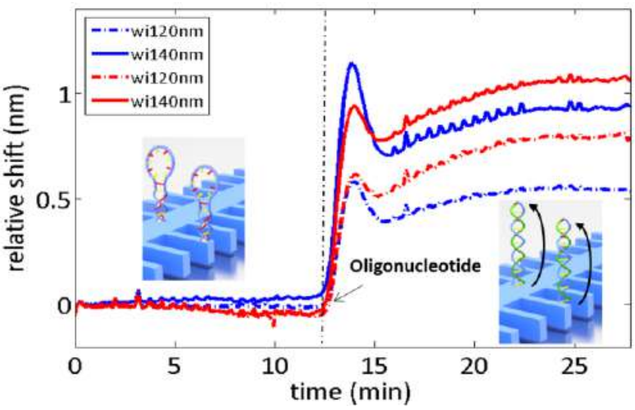

Figure 2: Spectral shifts of the PBG edge when the oligonucleotide detection takes place.

Control of Lamb Waves by Phononic Plates

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Any vibration in a thin elastic plate can be decomposed in three fundamental modes, which present different propagation characteristics, which suggest that the design of devices for their control have to be designed for a specific mode. We present here a summary of our recent works concerning the full control of elastic waves in thin structured plates. First, several devices for the control of flexural waves (A0 mode) will be discussed and analysed. It will be shown that the theory developed for the control of the A0 mode can also be applied to the control of the symmetric Lamb mode (S0 mode). Finally, a general approach to include the propagation of shear waves (SH0 mode) will be presented, showing how it is possible the design of refractive devices working simultaneously for all the three fundamental Lamb modes (see Fig.1).

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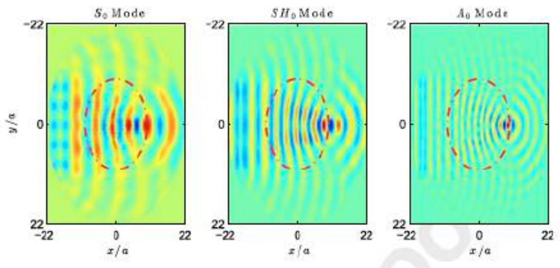

Figure 1: Luneburg lens designed to work simultaneously for the A0, S0 and SH0 modes.

Microscopic Origin of the Valley Hall Effect in Transition Metal Dichalcogenides

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The band structure of many semiconducting monolayer transition metal dichalcogenides (TMDs) possesses two degenerate valleys with equal and opposite Berry curvature. It has been predicted that, when illuminated with circularly polarized light, interband transitions generate an unbalanced nonequilibrium population of electrons and holes in these valleys, resulting in a finite Hall voltage at zero magnetic field when a current flows through the system. This is the so-called valley Hall effect that has recently been observed experimentally. Here, we show that this effect is mediated by photogenerated neutral excitons and charged trions and not by interband transitions generating independent electrons and holes. We further demonstrate an experimental strategy, based on wavelength dependent spatial mapping of the Hall voltage (see Figure 1), which allows the exciton and trion contributions to the valley Hall effect to be discriminated in the measurement. These results represent a significant step forward in our understanding of the microscopic origin of photoinduced valley Hall effect in semiconducting transition metal dichalcogenides and demonstrate experimentally that composite quasi-particles, such as trions, can also possess a finite Berry curvature.[1]

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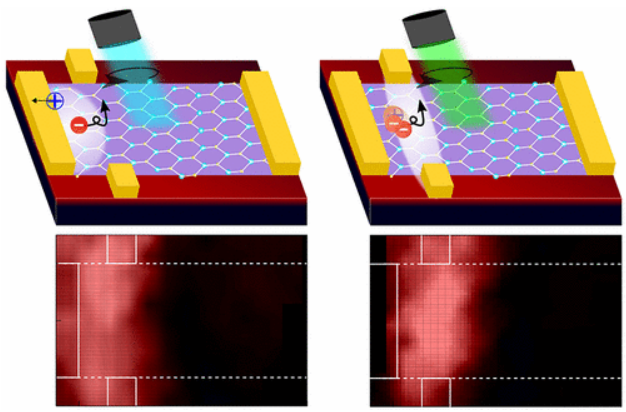

Figure 1: Schematic illustration of the experimental setup (top) and spatial dependent response of the Hall voltage of the valley Hall effect mediated by excitons (left) and trions (right).

Plasmonic nanoantennas for nanometer, picosecond control of VO_2 phase-transition

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Efficient and reversible switching of plasmonic modes at Vis and NIR wavelengths is one of the key desirable properties for optoelectronic devices. Phase-transition materials offer technologically relevant opportunities by providing notable changes in their dielectric response [1]. Vanadium dioxide (VO_2) is characterized by an insulator-to-metal transition at around 68°C [2]. In this work, we show how resonant pumping allows to use Au nanoantennas (NAs) fabricated on top of high-quality VO_2 films as a catalyzer for achieving ultrafast, highly localized VO_2 phase-transition [3]. Optical experiments demonstrate picosecond all-optical switching of the local phase transition in plasmonic NA-VO2 hybrids, exploiting strong resonant field enhancement and selective optical pumping in plasmonic hot-spots (Figure 1). The antena-assisted pumping mechanism is confirmed by numerical model calculations of the resonant, antenna-mediated local heating on a picosecond scale. Moreover, it is demonstrated that the phase transition mediated by local pumping of a plasmon resonance does not influence the resonance of a perpendicular NA positioned less than 100 nm away from the excited antenna. The NA-VO_2 hybrids enable new directions in all-optical ultrafast switching at picoJoule energy levels, and pave the way for plasmonic memristor-type devices exploiting nanoscale thermal memory.

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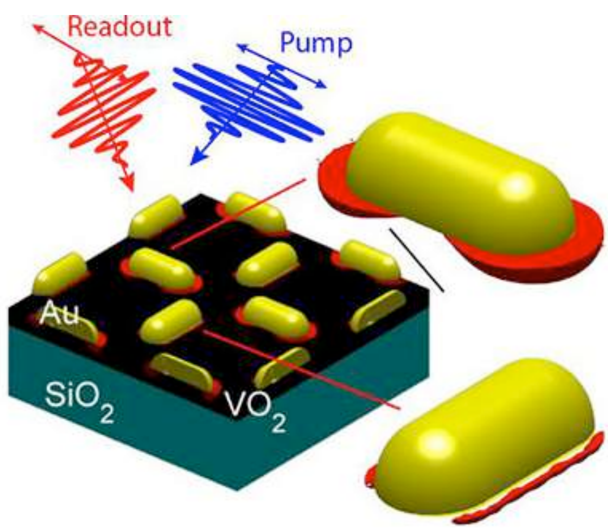

Figure 1: Pump-probe scheme of NA-VO_2 hybrids and simulated phase-switched hot-spots (red regions).

3PM2018 – POSTERS

Curved Laser Traps for Optical Manipulation of micro- and nanoparticles

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Optical tweezers, which use strongly focused point-like laser beams to manipulate small particles, have revolutionized our understanding of the microworld, providing techniques for cell and single-molecule studies, for microfabrication, and more. However, most efforts have focused on manipulating individual micro-objects generally ignoring the problem of optical transportation of particles en masse of both micro- and nanoparticles.

Using a totally different approach, we have developed an optical manipulation tool that allows mass light-driven transport of metallic and dielectric micro- and nanoparticles [1-2]. This freestyle optical trap [2] is created with a strongly focused laser beam in the form of an arbitrary 2D or 3D light curve, defining the particle trajectory. It exploits the optical forces arising from the beam's intensity and phase gradients for particle confinement and propulsion along the required trajectory. The developed non-iterative trap design technique allows for fast automatic reconfiguration of particle trajectory and speed—similar to robotic motion planning—to avoid contact with, or to impact on, objects in the host environment in the 2D [1] and 3D [3] cases.

We have demonstrated these functionalities experimentally on metallic plasmonic nanoparticles [1], even by using a resonant laser wavelength to provide both optical transport and heating of the particles simultaneously—a capability of special interest for targeted drug delivery, micro-scale photothermal therapy and nanolithography. This strategy is extendable to 3D trajectories as our recent results confirm [3]. Moreover, the application of these curved laser traps for opto-electric printing of plasmonic nanopariticles has been also exploited [4]. We envision that this new laser shaping technology will expand horizons in optical manipulation, light–material processing, micro/nano-fabrication and other applications yet to be explored.

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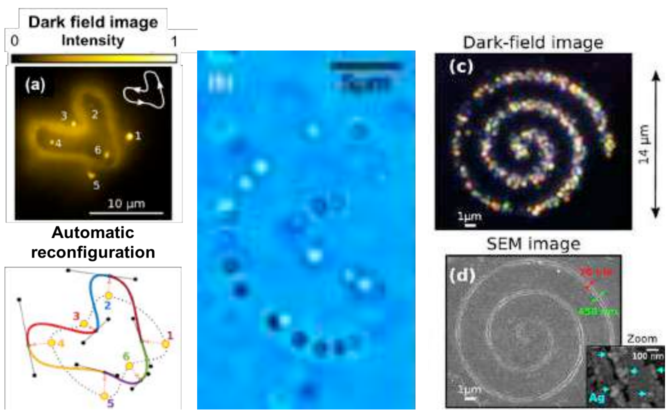

Figure 1: (a) Plasmonic nanoparticles, NPs, (100-nm-diameter gold spheres) are optically transported along reconfigurable 2D trajectories (time lapse image, see video online), following robotic motion planning based on Bézier paths. (b) Silica micro-particles (1000-nm-diameter) transported along reconfigurable and speed controlled 3D trajectory. Different particle appearance in the photogram indicates their axial position.
(c) Laser printing of silver NPs (40 nm) deposited on a transparent ITO electrode with freestyle trap. The color dark-filed image shows the light emitted by the silver NP assemblies created along an Archimedean spiral circuit, whose SEM image is displayed in (d). Zoom inset in (d) shows several subwavelength NP assemblies (≤150 nm).

Cosolvent-Assisted Assembly of Nanoparticles into Highly Regular Plasmonic Arrays

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The development of efficient plasmonic sensors requires fabrication processes for nanostructured substrates that show homogeneous optical properties over large-scale areas. As shown in Figures 1 and 2, regular arrays of 2 and 3-dimensional nanoparticle (NP) clusters of submicron size can be realized by nanopatterned templates. The periodicity, given by parameters *a* and *b*, determines the coupling between local plasmons and, moreover, may result in lattice plasmon resonances [1]. By varying the pattern geometry, such modes can be tuned to match desired wavelengths in the visible and near infrared [2]. Whereas preceding work focused on the fabrication of assemblies on comparatively small areas [3], we extend this process to large areas introducing ethanol as a cosolvent in the dispersion of polymer-coated Au NPs of different shapes. The composition of the dispersion dramatically changes the fluid dynamics of the NPs in the droplet [4]. In this study, we have varied systematically key parameters, such as the concentrations of alcohol, surfactant, and particles, to vary the emerging flow and to finally control the repartition of NPs in the droplet before applying the target substrate. As demonstrated in Figure 2, our approach strongly improves the homogeneity of the assembly yielding evenly sized and well-separated regular structures with high reproducibility. Reduction of defects and high uniformity over macroscopic dimensions enhances the plasmonic signal and paves the way for sensitive plasmonic sensing modules.

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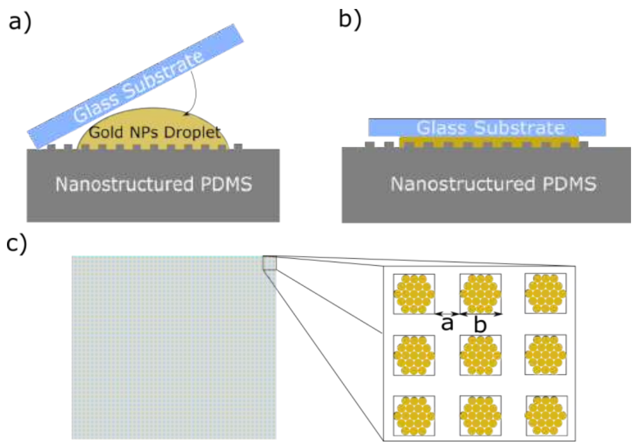

Figure 1: a) Schematic of processing Au NP arrays, b) drying process, c) gold NP assemblies on the substrate and some arrays zoomed in.

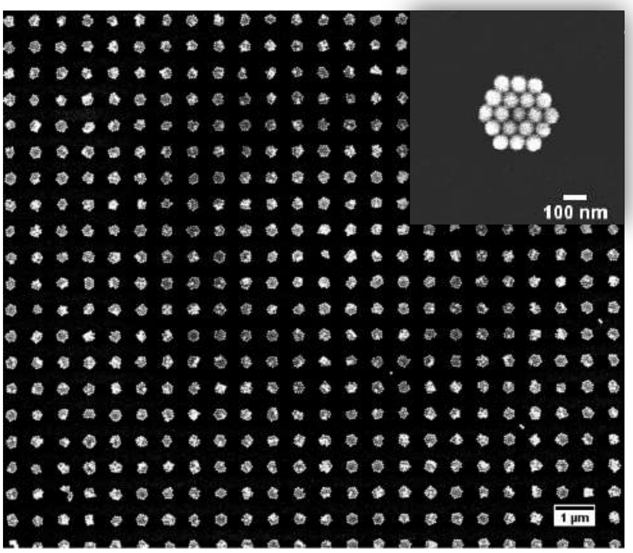

Figure 2: Electron microscopy image of an assembly of 65 nm spherical Au particles on glass.

Plasmonic of Ultra-Small Gold Nanoparticles in Quantum Regime

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Abstract

Nowadays, Plasmonic nanoparticles have attracted enormous attentions due to their reach scientific features and many technological applications in various fields [1]. Recently, many researchers have been focused on fabrication of monodispersed ultra-small gold nanoparticles and application of them in various fields including drug delivery, cancer treatment, biological imaging. In spite of the various experimental reports, there is no explicit theoretical study in the literatures to completely describe experimental optical properties of small gold nanoparticles in the range 3.0 to 15 nm. For nanoparticles with the sizes comparable or less than the mean free path of the electrons, using dielectric function of the bulk metal in the Mie theory usually provides incompatible results with experiments. Due to the surface scattering of electron movements in the ultra-small regime, quantum effects should be considered as a modification of the bulk dielectric function. In this research, we have proposed an analytical modification of the Drude dielectric model to obtain size dependent dielectric function and we have also calculated the optical properties of gold nanoparticles in the range of sizes from 3.6 nm to 20 nm. In this model, we have introduced a new size dependent plasma frequency, $\tilde{\omega}_p(R)$, for the free electrons with intraband transitions, which is different from the bulk plasma frequency. The functionality of this new surface plasma frequency on the size of the nanoparticle is obtained as $\tilde{\omega}_p(R)/\omega_p = a + b/R^2$ (Fig. 1). Comparison of the calculated extinction efficiency with the experiments [2, 3] shows the ability of this modified classical model to accurately describe the optical properties of ultra-small gold nanoparticles in the quantum regime.

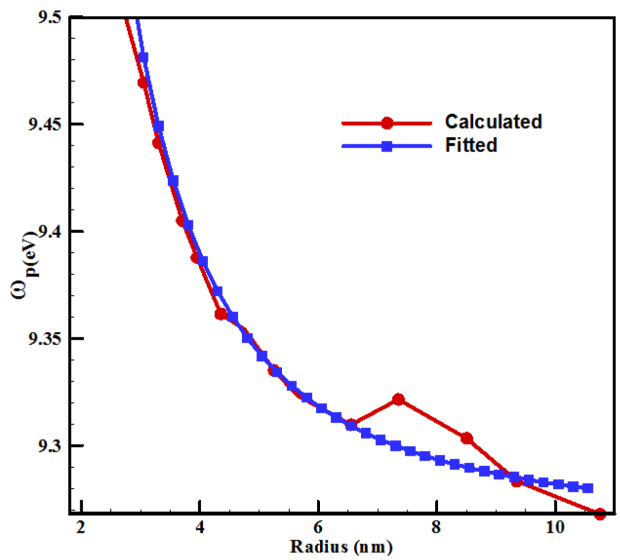

Figure 1: deviation of plasma frequency from bulk value with increasing of size.

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Franson Interference from the cascade transition in a quantum-dot–metal-nanoparticle hybrid system

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The manipulation of the Franson[1] two-photon interference emitted from a QD coupled to surface plasmon modes in the non-Markovian regime is investigated theoretically. The QD is considered as a three-level system in ladder configuration placed in the vicinity of a metal nanoparticle (MNP). Our main aim is to explore whether the interference and the joint count probability can be controlled via the geometrical parameters of the plasmon system. When light is confined using localized surface plasmons, the local density of states (LDOS) is altered significantly. As a result, the light-matter interaction can be significantly enhanced [2]. In the interaction picture and under the rotating-wave approximation the Hamiltonian is written as

$$\hat{H}_I^{\text{int}} = -[\hat{\sigma}_{21}\int_0^\infty d\omega' \vec{d}_{21}.\hat{E}(\vec{r}_d,\omega') + H.c.]$$

$$-[\hat{\sigma}_{32}\int_0^\infty d\omega \vec{d}_{32}.\hat{E}(\vec{r}_d,\omega) + H.c.]$$

Quantization of the electromagnetic fields in the presence of an absorbing and dispersive medium via dyadic Green's function approach leads to an expression for the electric field operator in the form [3]

$$\hat{E}(\vec{r},\omega) = i\sqrt{\frac{\hbar}{\pi\varepsilon_0}}\int d^3r' \frac{\omega^2}{c^2}\sqrt{\varepsilon_I(r',\omega)}\bar{G}(\vec{r},\vec{r}',\omega)\hat{f}(r',\omega).$$

The state of the system at time t by reduced amplitudes can be written as:

$$|\psi(t)\rangle = d_3(t)|3\rangle|\{0\}\rangle + \int_0^\infty d\omega d_2(\omega,t)|2\rangle|1(\omega)\rangle$$

$$+\int_0^\infty d\omega'\int_0^\infty d\omega d_1(\omega',\omega,t)|1\rangle|1(\omega')1(\omega)\rangle.$$

Here, in all terms, the first ket indicates the state of the QD and the second ket shows the induced plasmon mode excitation. induced plasmon modes. The two-photon state produced by cascade emission is given by the entangled state as

$$|\psi(\infty)\rangle = \int_0^\infty d\omega'\int_0^\infty d\omega d_1(\omega',\omega,\infty)|1(\omega')1(\omega)\rangle.$$

The radiation reaches the detectors D_1 and D_2 via short and long optical paths of lengths S and L. The positive part of electromagnetic field in each detector is determined by: $\frac{1}{2}[\hat{E}^{(+)}(S_i,t_i)+\hat{E}^{(+)}(L_i,t_i)]$.

Possibility of two-photon interference, by measuring the joint probability is

$$P_{12} =$$
$$\int dt_1\int dt_2 \langle\psi|\hat{E}^{(-)}(r_1,t_1)\hat{E}^{(-)}(r_2,t_2)\hat{E}^{(+)}(r_2,t_2)\hat{E}^{(+)}(r_1,t_1)|\psi\rangle.$$

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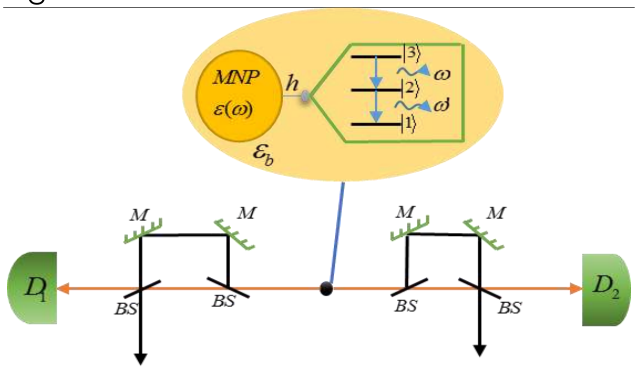

Figure 1: Schematic illustration of the QD-MNP hybrid system. D_1 and D_2 are photodetectors.

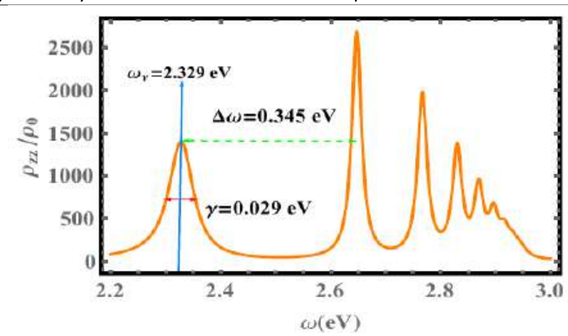

Figure 2: scaled LDOS, ρ_{zz}/ρ_0, versus frequency for a 10 nm Ag nanosphere when h=5 nm. Here, ε_b =5.4 and ρ_0 is the free space DOS.

Biocomposites in food packaging, water remediation and wound management

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The increasing volumes of plastic wastes that are accumulating in our planet are making more and more necessary the use of alternative naturally-derived and/or biodegradable polymeric materials. Here we will present fully biodegradable biocomposites that derive from natural resources like polysaccharides by vegetable wastes or proteins by animals. The preparation of the biocomposites is done with green methods, that among other advantages, they reassure that the intrinsic properties of the starting materials are transferred to the final biocomposites. In this way we can obtain biocomposites with antioxidant, antibacterial or anti-inflammatory properties. On the top, we can tune the biodegradation time of the developed materials, in order to control the delivery of active principles they incorporate to their adjacent environment.

Using the abovementioned materials and techniques, we engineer biocomposites that can be used either as active food packaging materials or in water remediation applications or finally in would management for protection and active healing. Some examples of the materials that will be presented in this conference follow: For food packaging applications we produce biocomposites of biodegradable polymers (i.e. PLA, PDMS, PCL, PVA, Starch, etc.) with high loading of vegetable wastes (coca shell, orange peel, parsley stems, spent coffee, etc.) that are prepared by extrusion and injection molding techniques, easily scalable for high volumes production. [1] These materials are approved for food contact, can protect the food due to high oxygen barrier properties and in some cases also due to antioxidant action. For water remediation we use biocomposites of bioplastics, like silk fibroin, or keratin combined with vegetable wastes, like orange peel or spent coffee, in order to develop foams that can interact with water and adsorb pollutants like heavy metals, oily substances, or dyes (Figure 1). [2] Finally, for the development of active scaffolds for protection and active healing of wounds we develop biocomposites by natural matrices, like alginates, silk fibroin, hyaluronic acid, keratin, etc. and we tune their degradation time while in contact with the wounds, in order to deliver in controlled times active principles, like drugs or natural antioxidant or antibacterial agents.

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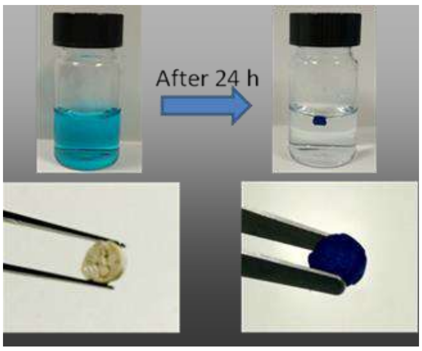

Figure 1: Biocomposite foam with orange peel for efficient dyes removal from water

Are Nanoreinforced Natural Fibre Composites the Route Forward?

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Renewable polymers often have inferior properties to their synthetic counterparts against which they have to compete. The development of composites is thus a vital strategy for enhancing the performance of these polymers. To create a new generation of renewable polymer matrix composites, it is also necessary to replace synthetic fillers with renewable ones – hence the re-emergence of natural fibre composites. Renewable or green composites, also often called biocomposites, have regained vast interest in the past decades because of the wide availability of natural fibres, the increased availability of renewable polymers and the biodegradability of the composites.
Natural fibres are already being considered for various applications. Advantages of natural fibres are their low cost, low density, renewability and biodegradability. The main drawbacks are inconsistency in mechanical properties, relatively low tensile strength, and their limited thermal stability resulting in a limited processing routes. The increased availability of nanocellulose, which can be produced top down by the mechanical disintegration/fibrillation of (chemically modified) cellulosic fibres or bottom up by microbial fermentation of suitable carbon sources. These new reinforcing agents may provide a breakthrough in the development of green composites by introducing an additional nanoscale reinforcement into the matrix of traditional natural fibre composites. This should allow for the development of novel composites with much improved properties. We focused on bacterial cellulose (BC), because it's the purest cellulose. BC fibrils have diameters ranging from 10 to 100 nm and a measured Young's modulus of 114 GPa. In addition to its light-weight and attractive mechanical properties, bacterial cellulose is non-toxic, renewable and biodegradable. These intrinsic properties can be used to influence and enhance the surrounding polymer matrix performance.
Nature demonstrates the use of hierarchical structures when high mechanical resistance is needed, e.g. in plant cell walls, animal shells and bones, through the assembly of molecules of different sizes. The application of this concept is markedly improving our engineering of truly green composites. Nanocellulose coated natural fibres were created by cultivating cellulose-producing bacteria in the presence of fibres or by fibre coating resulting in significant coverage of the fibre surfaces by bacterial cellulose. We have created hierarchical structures in natural fibre composites by using these "hairy" fibres to deliver the nanoreinforcement into polymer matrices avoiding troublesome processing issues associated with anisotropic nanofillers. There are many outstanding issues in hierarchically structuring composites: the compatibility between all phases, the arrangement of the nanofiller within the composite, and biodegradability control. The separation of end-of-life waste of truly green composites from the waste streams and compositing is another thorny issue.

Talga: Emerging high quality scalable graphene supply; path to high performance low eco impact multi-functional product applications

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With its impermeable and conductive nature graphene can replace nano-additives currently used in various applications [1-3]. The current bottlenecks in graphene commercialisation is the availability of large volume, cost-effective high quality few layer graphene/Graphene nano platelets and its effective incorporation. Talga has the capability and resources to bring graphene into the market in big volume with its cost effective industrially scalable process. Further Talga developed technology helps to overcome the compatibility issues by customising dispersion chemistry for graphene to suit existing commercial products.

Coatings & composites may prove to be the most significant demand drivers for graphene in terms of volume consumption and speed to market and Talga made a significant progress in utilisation of Talga electrochemically expanded graphene nano platelets (GNP) & few layer graphene in various advanced coatings / composite products. Technology advancements made and challenges faces during these developments in the areas of coating, composite, energy & building materials will be discussed.

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Accessing low energy glasses by polymer nanostructuring

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A thermodynamic system in nonequilibrium spontaneously tends to decrease its free energy to the most stable state. However, nonequilibrium systems are ubiquitous in nature due to the fact that the time scale to reach the lowest free energy state is too long compared to a given observation time (e.g. the human life). Glasses belong to the category of nonequilibrium systems. In this case, the closest accessible free energy minimum is the supercooled liquid in metastable equilibrium. The evolution of the thermodynamic state of a glass toward equilibrium is known as physical aging [1,2]. In bulk glasses, accessing the supercooled liquid equilibrium state requires experimentally unfeasible time scales already at temperature not too far from the glass transition temperature (Tg). Such a kinetic limitation prevents the knowledge of the fate of thermodynamics at temperatures considerably lower than Tg in bulk glasses.
In this contribution, I will show how nanostructuring of polymer glasses induces an acceleration of the rate of equilibrium recovery [3,4]. Several examples in this sense, including polymer nanocomposites, thin films and nanospheres, will be provided. As a showcase, Figure 1 shows the evolution of the enthalpy with aging time for a series of poly(methyl methacrylate) (PMMA)/silica nanocomposites [5]. As illustrated, equilibrium recovery proceeds faster in nanocomposites with larger silica content.
In the last part of the talk, it is shown how the acceleration of physical aging in nanostructured glasses constitutes a formidable mean to access information of utmost importance on the thermodynamics of glasses. In particular, showing physical aging results on 30 nm thick polystyrene films, it is demonstrated that a glass with the same entropy as that of the corresponding crystal can be obtained. This result solves a 70 years problem on the existence of the so-called "ideal" glass [6].

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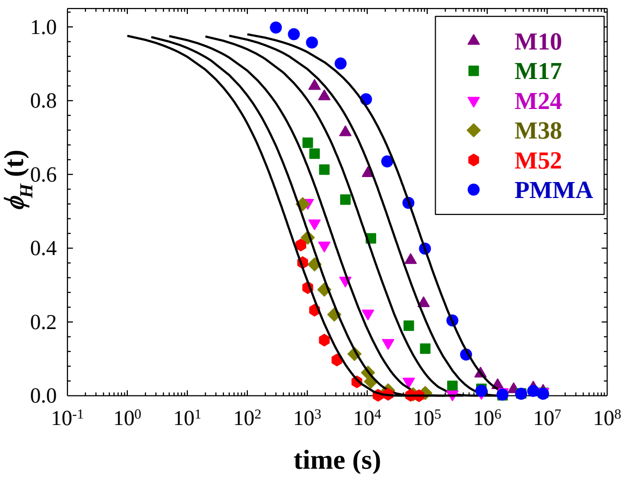

Figure 1: Enthalpy recovery function for PMMA/silica with concentration 10 (M10), 17 (M17), 24 (M24), 38 (M38), and 52 (M52) wt. % of silica, and pure PMMA [5]

Structure Evolution and Control in Graphene Polymer Composites

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Graphene and related 2D materials have extraordinary physical properties that along with their high aspect ratio make them excellent candidate filler materials for polymer nanocomposites, capable of producing significant gains in material properties at extremely low concentrations. We have recently investigated the conformations of polymer chains in polymer–graphene nanocomposites, and have shown that the chains have a reduced radius of gyration, and reduction in interchain entanglements, that is consistent with confinement at a solid interface.[1] We have also discovered that when we look at the graphene filler we find, using scattering techniques, that the host polymer matrix can influence the morphology of the graphene.[2] With both of these in mind we have turned our attention to the processing of graphene polymer composites. Reliable processing of such materials with uniform and consistent properties remains a significant challenge because of the difficulty in controlling the graphene conformation and dispersion. Using shear rate and shear history we can control graphene network morphology and nanocomposite properties. Remarkable changes in electrical impedance unique to composites of graphene nanoplates (GNPs) are observed. Low shear rates ≤ 0.1 s^{-1} break up the typical GNP agglomerates found in graphene composites, partially exfoliate the GNPs to fewer graphene layers and reduce orientation, enhancing electrical conductivity in the composite materials. Whereas, at higher shear rates GNP orientation increases and the conductivity reduces by four orders of magnitude, as the graphene filler network is broken down. Interestingly the structure of the composite continues to evolve over time, reflected in further changes in conductivity, after the shear force has been removed and the process temperature maintained, figure 1. This work provides critical insights for understanding and controlling GNP orientation and dispersion within composites and will have important consequences in the industrial processing of graphene polymer composites via the informed design and choice of processing.

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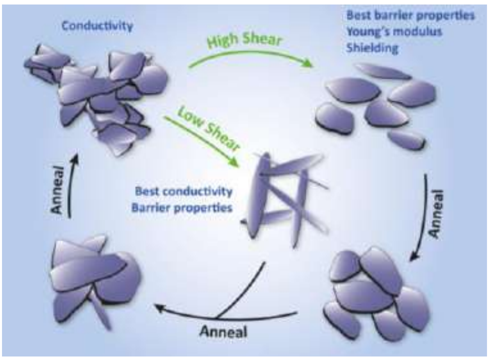

Figure 1: Schematic of processing effects on the GNP structure within the composite

Ionic Liquids: versatility and potential as interfacial agents for designing physicochemical interactions and tailoring morphology and properties of nanofilled polymers.

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The design of nanostructured polymers is an important issue for the use of polymer-based materials in high-value industrial applications. Among these polymer-based nanomaterials, the design of an inorganic-rich nanostructure could be a relevant solution allowing the combination of properties of both organic and inorganic components as well as the unexpected properties of matter at nanoscale.

Interfaces and resulting interphases are key components for many multifunctional materials and even more particularly for nanomaterials such as nanocomposites according to the large amount of deployed surface of contact in between phases due to nanosize objects. Very recently, Ionic liquids (ILs) are become attractive additives as interfacial agents thanks to their excellent physico-chemical properties such as low volatility, non-flammability, good ionic conductivity, excellent thermal stability as well as their ability to tune their affinity towards the polymer matrix by the control of the chemical nature of the counter-anion and/or the cation. Such interactions involve a wide variety of bonding mechanisms and energies resulting in organic-inorganic materials of variable stability and reactivity.

The lecture will describe different routes proposed to design the interphase and will underline i/ the role of the design of the molecular architecture of ILs in order to control the polymer-IL-nanofillers interactions and *ii*/ the needs of proper physico-chemical characterization techniques to investigate the fundamental mechanisms and to analyze the resulting nanostructures in order to establish microstructure-properties relationships.

Several examples of ionic liquids modified nanofillers-polymer combinations will be detailed to design polymer nanomaterials from : i) layered silicates involving electrostatic interactions with ammonium, phosphonium, or imidazolium-based ionic liquids , ii) colloidal silica particles on which covalent bonds are possible through the use of silylated ionic liquids or iii) only Π–Π intermolecular interactions between graphene and ionic liquid. A last route will be described from the introduction of metal-oxo clusters, such as organo-functional polyhedralsilsesquioxanes modified by ionic liquids to lead O/I networks synthesized under thermal conditions or UV exposure.

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Nanoparticles from biological source and polymer nanocomposites

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Unexpected and attractive properties can be observed when decreasing the size of a material down to the nanoscale. Polysaccharides, an important class of biological polymers, are no exception to the rule. In addition, structural polysaccharides, such as cellulose and chitin, or storage polysaccharides, such as starch, have a highly reactive surface resulting from the high density of hydroxyl groups which is exacerbated at this scale. As is usually the case when a new field is developing, the terminology is somewhat confused, but the term "nanocellulose" is now used to cover the range of materials derived from cellulose with at least one dimension in the nanometer range. Different forms of cellulose nanomaterials, resulting from a top-down deconstructing strategy (cellulose nanocrystals-CNC, cellulose nanofibrils-CNF) or bottom-up strategy (bacterial cellulose) can be prepared [1]. Strong acid hydrolysis of cellulose fibers, a process reported in the 1940s [2], is generally used to isolate CNC (Fig. 1a). A top-down mechanically-induced destructuration of cellulose fibers can be induced by submitting slurries to high shear forces to release more or less individual CNF (Fig. 1b), as described in the 1980s [3]. These nanomaterials have been academic curiosities for many years. There is today a substantial amount of research on these cellulosic nanomaterials, and commercial development is underway with some promising applications. These include paper and cardboard industry, use as reinforcement for nanocomposites, basis for low-density foams, additive in adhesives and paints, as well as a wide variety of filtration, electronic, food, hygiene, cosmetic, and medical products.

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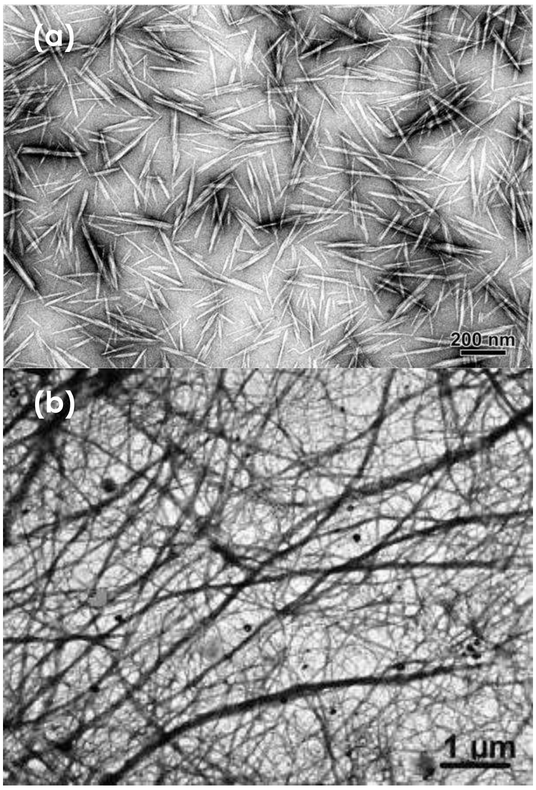

Figure 1: TEM from a dilute suspension of (a) CNC extracted from ramie [4], and (b) CNF prepared from *Opuntia ficus-indica* [5].

Green Nanotechnology: aims and expedients

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Green nanotechnology aims to develop clean technologies to minimize potential environmental and human health risks associated with the manufacture and use of nanotechnology products, and to encourage replacement of existing products with new nanomaterials that are more environmentally friendly. The most important component of nanotechnology is nanomaterials, i.e. materials with the ordered structure of their nanofragments having size from 1 to 100 nm. The production and process aspects of green nanotechnology involve both making nanomaterials in a more environmentally benign fashion and using nanomaterials to make current chemical processes more environmentally acceptable. The paper contains information about advanced nanomaterials can be produced without harming the environment or human health. This encompasses the production of nanomaterials without environmental toxicity, at room temperature and with the use of renewable energy sources. The paper contains the descriptions and results of theoretical and experimental researches in the field of environment friendly nanotechnology carried out over the past decade by scientific team of company Polymate Ltd.-International Nanotechnology Center

Multi-functional CVD graphene/polymer nanolaminates

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Abstract

Graphene has been termed the stiffest and strongest material known to date. Given its superior mechanical behaviour, combined with exceptional electrical and thermal properties, graphene is the ideal material for lightweight, high strength composite materials with several multi-functionalities. So far, only graphene in a form of separated flakes, i.e. nanoplatelets (GNPs), has been adopted for the production of composites for large scale applications. However, the actual mechanical performance of GNP composites are still below the expectations due to the small lateral size of GNPs that results in poor transfer of stresses from the polymer matrix. Other –typical- limitations are due the difficulties of graphene dispersion and flake orientation in order to enhance the mechanical properties of commercial resins. The use of large-size graphene growth via Chemical Vapour Deposition (CVD) can overcome the aforementioned drawbacks by offering (a) large lateral size of continuous graphene and thus efficient stress transfer, (b) uniform and controllable dispersion in the polymer matrix, and (c) controllable mechanical, electrical and thermal properties. The use of CVD graphene as reinforcement in polymer laminates has been recently proposed [1, 2]; however, due to criticalities in manipulating ultra-thin CVD graphene/polymer plies, the maximum graphene content that could be achieved was very small (less than 0.2%). Here, we propose a novel bottom-up approach for the production of macro-scale CVD graphene/polymer nanolaminates based on the combination of ultra-thin polymer casting, wet transfer and floating deposition. By casting ultra-thin polymer films (<50 nm), higher graphene volume fractions can be achieved (up to 0.66%) and the resulting nanolaminates (at the macroscale) have the potential to outperform the current state-of-the-art graphene-based composite materials in both mechanical property and electrical conductivity enhancements (~ 60 S/cm).

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Figures

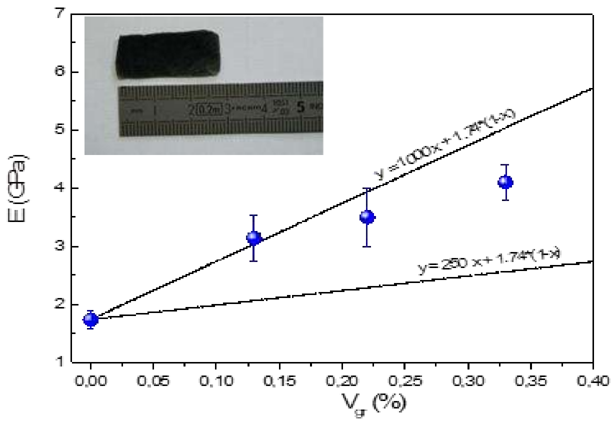

Figure 1: Young modulus of the nanolaminates as a function of graphene content. Inset: Photograph of a produced nanolaminate with 0.66% CVD graphene (b)

Functional applications ZnO tetrapod nanomaterials made by flame transport synthesis

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Abstract

Applications of ZnO tetrapods in: (i) Nanoelectronics, (ii) Optics, (iii) Advanced Composites, (iv) Sensing, (v) 3D Nanocarbons, (vi) Biomedical, and in many other directions [1-10] will be briefly presented in this talk.

Zinc oxide (ZnO) material with n-type conductivity, wide bandgap of ~3.37 eV, hexagonal-wurtzite crystal structure, has been among one of the most pioneering materials towards nanostructuring and broad range of applications [1]. A wide variety of nanostructural shapes from ZnO have been synthesized and utilized for many applications but the role of structural aspects, such as complex shape, still needs to be addressed. Inspired by unique capabilities of ZnO, we recently developed a flame based nanostructuring process, called flame transport synthesis, which offers very simple and mass-scale fabrication of tetrapod shaped ZnO structures. The 3D shape feature enables these tetrapods to be used as unique building blocks for fabricating highly porous and flexible ceramic materials for advanced technologies. They can be used as backbones/templates for synthesizing hybrid and new 3D porous nanomaterials [1-10]. The applications and nanostructuring opportunities by flame approach are briefed in Figure 1.

The presentation will highlight:

- Scopes of ZnO nanomaterials towards various applications.
- Nanostructuring by flame transport synthesis approach.
- Importance of tetrapod and other complex shapes towards applications.
- Highly porous 3D nanomaterials as flexible ceramic materials.
- Template based nanostructuring for new 3D nanomaterials.

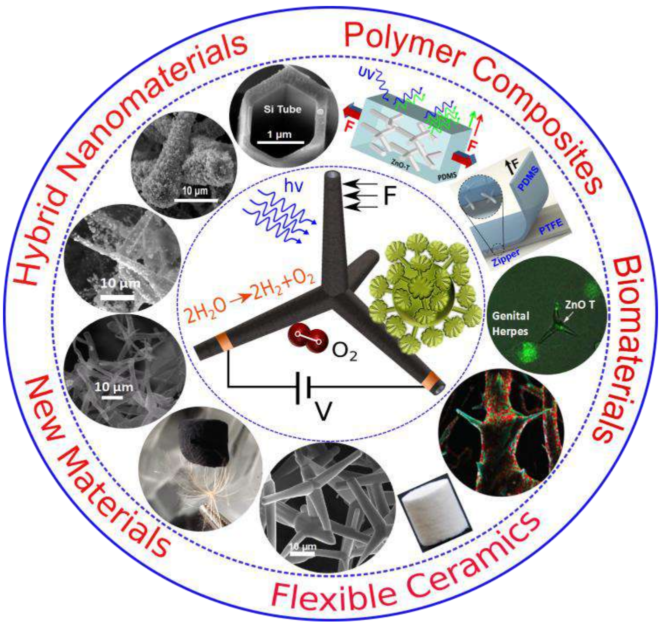

Figure 1: Application scopes of ZnO tetrapod shaped nanostructures in various directions.

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High Throughput Electrospinning and Electrospraying for the Design of Innovative Nanomaterials and Structures of Application Interest

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Abstract

Looking genuinely at nature, nanofibers often serve as a basic platform where either organic or inorganic components are built upon. For instance, cellulose nanofibers would represent the building block in plants while collagen nanofibers in the animal body. Electrospinning is a physical process used for the formation of ultrathin fibers by subjecting a polymer solution to high electric fields. At a critical high voltage, the polymer solution droplet at the tip of the injector distorts and forms a Taylor cone to be ejected as a charged polymer jet. This stretches and is accelerated by the electrical field towards a grounded and oppositely-charged collector. As the jet travels through the electric field, the solvent completely evaporates. This results in the creation of ultrathin polymer fibers in a process called electrospinning or in particles in a process called electrospraying (1,5).

Since recently this process has been scaled up to an industrial level by companies such as Bioinicia S.L. and it is now possible to form materials and composites in larger volumes.

The current paper will highlight some recent advances carried out within our research group in which various applications of the high throughput electro-hydrodynamic processing technique making use of biopolymers and biopolymeric blends will be reviewed. These include examples in which new nanocomposites, coatings, multilayers, antimicrobial and bioactive nanostructured materials and encapsulates were successfully developed with application interest in packaging, biomedical, pharmaceutical and food fortification applications, respectively.

Acknowledgements:

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Multifunctional Properties of Rubber Nanocomposites

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Abstract

Rubbers, or most specifically called elastomers, are one of the most important commercial polymers for several applications in many sectors, such as automotive, industrial, packaging, healthcare and many others. They are formed by long chains with high molecular weights crosslinked at many points giving rise to the formation of a three-dimensional network structure. Their general characteristics involve elastic behaviour and high reversible deformation properties. The material recovers its original form once releases the stress that deform it.
The elastomers are soft and weak materials with a low modulus and strength. They usually require the inclusion of fillers to improve the physical and mechanical properties of the compound. However, a minimum of 30–40 wt.% of conventional fillers such as carbon black or silica is needed to increase the properties, but, this high concentration reduces the processability of the compound and increases the weight of the material, limiting their applications.
Nanocomposites offer the possibility for new paradigms of material properties. Due to their nanometer phase dimensions, polymer nanocomposites exhibit unique properties even by the addition of small amount of filler, not shared by conventional composites. The inclusion of carbon nanoparticles, carbon nanotubes or graphene, produces a multifunctional material, since not only increases the mechanical behaviour but also provides particular properties such as electrical and thermal conductivity, barrier properties, thermal stability, etc [1-3]. The stronger filler/matrix interaction at the interface leads to a more immobilized rubber shell compared with filler particles of micro dimensions.
Potential applications of carbon nanoparticles filled elastomer composites can be as sensing devices, electrical shielding and electrical heating equipments.

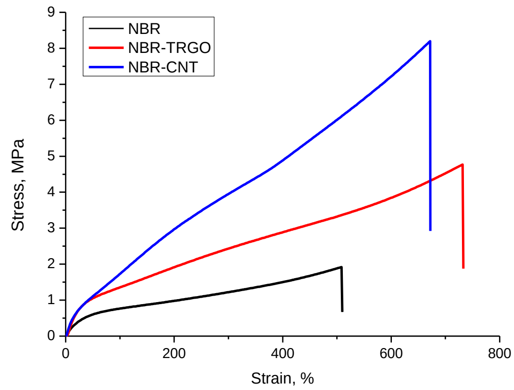

Figure 1: Stress-strain curves of carbon nanoparticles-NBR nanocomposites

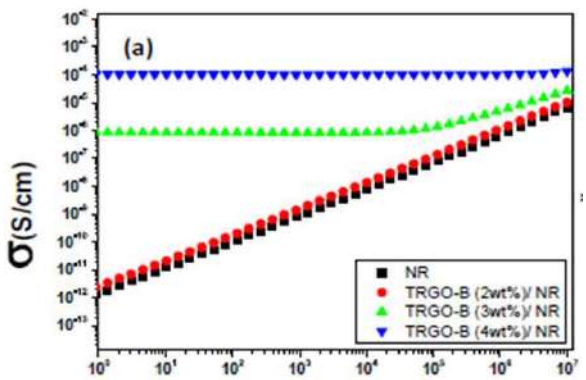

Figure 2: Electrical conductivity of graphene-natural rubber nanocomposites

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Electroactive polymer composites for bioelectronics

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Ionic and electronic conductive polymers show a great interest in the field of bioelectronics, at the interface between electronics and biology. This is due to its excellent capability to actively participate in different devices which convert ionic signals into electronic signals (and *vice versa*). [1] Moreover, their soft nature, charge transport and composition allow them to integrate well with both the solid substrate as well as the living tissue. So far, most of the polymers used by the bioelectronics community are based on commercial availability of polymers developed for devices such as OLEDs, transistors or solar cells.

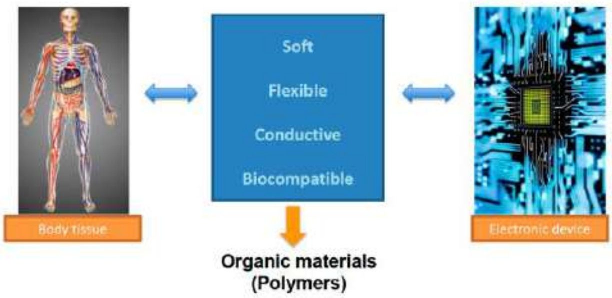

Figure 1: Organic bioelectronics demands new materials

In this presentation we will show our efforts and activities in the development of tailored conducting polymers and composite for bioelectronic devices. Emerging applications of these materials require new combination of properties such as high ionic or (electronic)conductivity, printability, biodegradability, compatibility with the electrodes/biological tissue or mechanical properties. Our activities include on the one hand new electronic conducting PEDOTs including low temperature cross-linked materials or more biocompatible films than PEDOT/PSS [2-4] On the other hand, soft ion conducting polymer electrolytes based on iongels and biodegradable polymers will be also presented. The final application of these innovative polymers in several devices such as organic transistors, light-emitting devices and electrodes for electrophysiology will be shown [5-6].

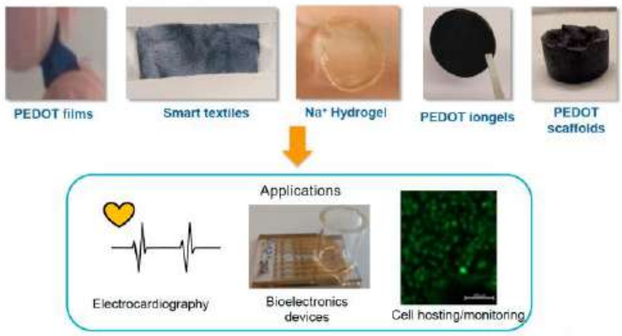

Figure 2: Innovative materials and applications

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Graphene-based materials for large-scale applications: ideal graphene vs. real commercial products

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Bulk composites are currently the most common, commercially available applications of graphene and related materials (GRM). The number of products containing these composites is increasing continuously, from tennis rackets to bicycles to skis. However, the lack of a clear metrology and of quality control for graphene is creating confusion among industrial end-users, [1,2] with some companies advertising as "graphene" what instead is graphite powders, platelets or other carbon materials. Whilst nomenclature[3] and a classification framework[4] have been proposed for 2D graphene-based materials, a clear agreement on international standards is still missing.
A high number of graphene producers worldwide s GRM with a very broad range of morphology and quality. It is thus difficult to evaluate correctly if the new materials continuously introduced on the market are truly competitive with commercially available ones, either in performance or in production cost.
To develop innovative and industrially relevant applications of GRM it is fundamental to have a realistic evaluation of the state-of-the-art of existing commercialized products. To this aim, here we describe a procedure to benchmark GRM materials available as commercial products from industrial producers worldwide.

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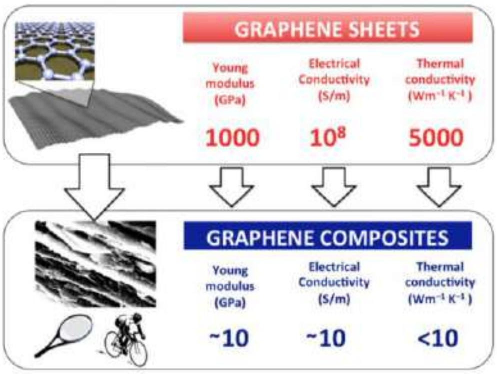

Figure 1: Schematic representation of the difference in performance between single, 'ideal' graphene sheets and graphene-based macroscopic composites suitable for commercial applications. From ref. [1]

Bacterial Nanocellulose: Surface Microstructuration and Composites

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Cellulose is a non-toxic, degradable and almost inexhaustible biopolymer expected to play a strategic role in replacing petroleum-based polymers. Nanocelluloses are gathering growing interest because they combine the properties of the cellulose (hydrophilicity, semi-crystalline fibrous morphologies, broad chemical modification capacity,…) with the high surface area of nanomaterials. Although cellulose is primarily obtained from plants, it can also be synthesized by bacteria, algae and fungi (Figure 1). In particular, bacterial nanocellulose (BNC) produced by microbial fermentation has the same molecular formula as plant-derived cellulose but, in contrast, is a pure biopolymer that exhibits a high degree of polymerization and crystallinity. Other distinctive features of BNC are: i) this nanocellulose can be manufactured under laboratory and pilot-plants conditions, ii) the control of cellulose topography and morphology can be attained during biosynthesis or iii) unique features can be introduced by combining cellulose characteristics with nanomaterials properties [1]

We have exploited several of such features to create advanced functional materials. Firstly, a strategy to control morphology and surface structuration of BNC films during biosynthesis will be described. Large areas with good replication of the stamp topographies down to few micron sizes have been achieved. Secondly, we will show some original routes to afford functional BNC nanocomposites by anchoring inorganic nanocrystals on the cellulose fibers and assemble "millefeuille" layered constructs [2,3] (Figure 2).

Performance of these nanocomposites in photocatalytic reactions and as a transportable culture platform for adherent mammalian cells will be presented.

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Figures

Figure 1: Sea squirt Ciona intestinalis, vase tunicate, with a cellulose exoskeleton. S. Siebert, Science in School Issue 41(2017).

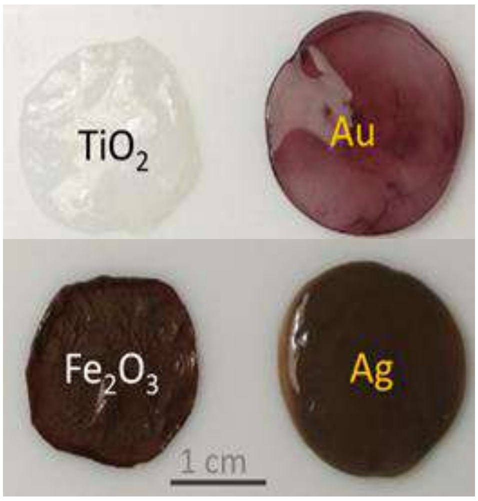

Figure 2: Bacterial nanocellulose composited with metal oxide and metal nanoparticles.

Block Copolymer-Based Nanocomposite Films: Hierarchical Structures by Chemical Design

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Organizing metal and semiconductor nanoparticles into ordered arrays with nanoscale structure represents a major challenge in nanotechnology, and bears the potential to advance applications such as sensing and photovoltaics beyond their current performance limits.

A highly modular approach for organizing nanoparticles into ordered structures involves the utilization of block copolymers. Block copolymers consist of different sequences of chemically distinct repeat units, and spontaneously form periodic nanoscale structures by microphase separation. Tailoring the chemistry of the nanoparticle's protecting monolayer to be compatible with one block of the polymer enables harnessing the inherent structure of the block copolymer to order the nanoparticles. Nanocomposite films prepared by blending such nanoparticles with block copolymers feature periodic structures, in which nanoparticles reside in alternating domains.

The presentation will describe design principles and discuss the main factors that govern nanoparticle-block copolymer assembly in thin nanocomposite films. Questions that will be addressed are:

- How can we control the **internal nanoparticle structure** inside a domain?
- How the nanoparticle **shape** influences the overall morphology?
- How can we use **block copolymer architecture** to further enhance nanoparticle ordering?

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Nanostructured fibres and fabrics for structural supercapacitor composites

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There is an ever increasing interest in multifunctional materials such as energy managing devices that have non-conventional mechanical properties. These include supercapacitors and batteries that are flexible, stretchable, tough and ultimately, that have structural properties. In particular, there is a great potential in exploiting the inherent layered structure of these devices in a structural composite architecture. In the context of structural supercapacitors, the two main challenges are: increasing the intrinsically low surface area of carbon fibre ($0.2m^2/g$), and producing a solid electrolyte with both high stiffness and ionic conductivity. This work introduces macroscopic fibres and fabrics of carbon nanotubes (CNT) as an attractive component for structural supercapacitors. The fibres have electrical conductivity above steel, tensile properties in the high-performance range, and more importantly a large surface area (250m2/g). CNT fibre unidirectional fabrics can be pressed with a thermoplastic polyelectrolyte to produce large ($100cm^2$) all-solid supercapacitors with specific power and energy densities as high as 46kW/Kg and 11.4Wh/Kg, with > 97% stability after 10000 charge-discharge cycles at 3.5V. The devices preserve these properties while bent 180° and have specific tensile strength above that of copper (40 MPa/SG). The talk presents recent progress in introducing these high energy-density films in laminate CF/epoxy composites to produce a hierarchical multifunctional structure. Galvanostatic charge-discharge (CD) measurements are performed *in situ* during during the mechanical tests give an indication that the limits of electrochemical operation comply with the expected deformations of the laminates in a structural element. Finally, figures of merit for multifunctionality are presented to compare results with the state-of-the-art and evaluate prospects for improvement by introduction Faradaic reactions.

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Figures

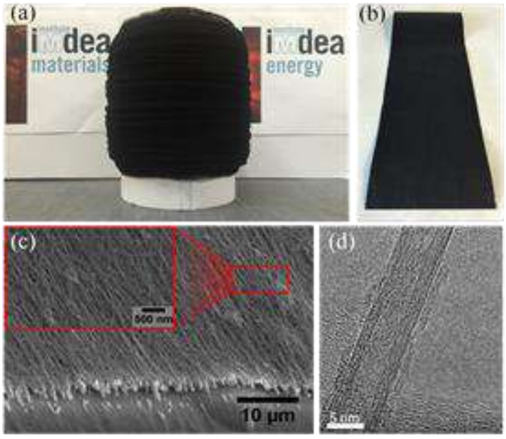

Figure 1: CNT fiber sheet electrode

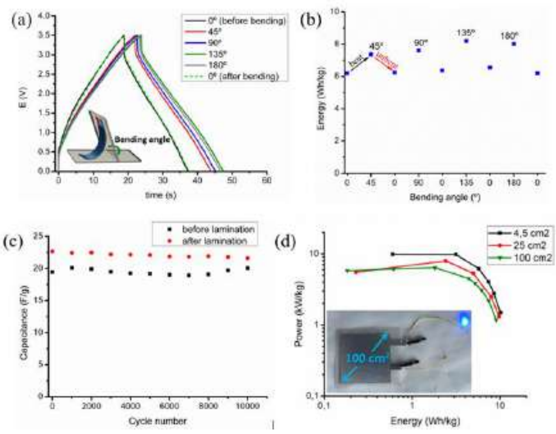

Figure 2: Electrochemical properties of devices and operation of devices under bending.

The Mechanics of Reinforcement of Nanocomposites by 2D Materials

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A detailed study has been undertaken of the mechanisms of stress transfer in polymeric matrices with different values of Young's modulus, E_m, reinforced by graphene nanoplatelets (GNPs) (Figure 1). For each material, the Young's modulus of the graphene filler, E_f, has been determined using the rule of mixtures and it is found to scale with the value of E_m. A theory has been developed to predict the stiffness of the bulk nanocomposites from the mechanics of stress transfer from the matrix to the GNP reinforcement based upon the shear-lag deformation of individual graphene nanoplatelets and the results are plotted in Figure 2. Overall it is found that it is only possible to realise the theoretical Young's modulus of graphene of 1.05 TPa for discontinuous nanoplatelets as E_m approaches 1 TPa; the effective modulus of the reinforcement will always be less for lower values of E_m. For flexible polymeric matrices the level of reinforcement is independent of the graphene Young's modulus and, in general, the best reinforcement will be obtained in nanocomposites with strong graphene-polymer interfaces and aligned nanoplatelets with high aspect ratios.

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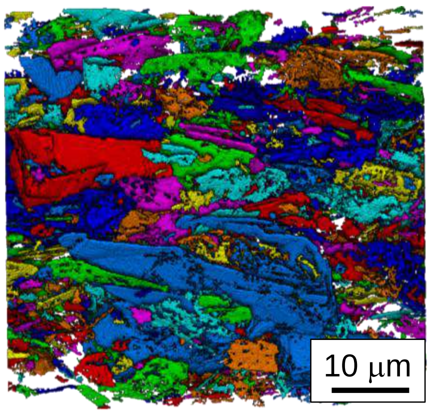

Figure 1: Artificially-coloured image of a CT scan of a natural rubber nanocomposite [2] containing M25 GNPs nanoplatelelets.

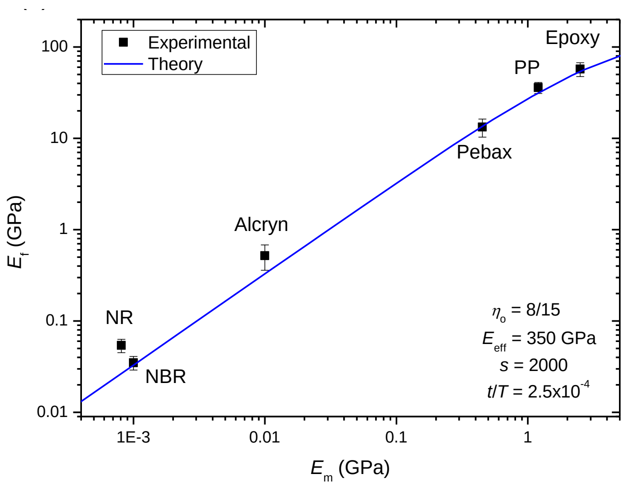

Figure 2: Variation of E_f with E_m for the M25 GNPs reinforcing a series of polymeric matrix different materials with different values of matrix modulus, E_m. The solid line is the behaviour predicted with the parameters indicated.

On the Nature of Microscopic Heat Carriers in Nano-Porous Silicon

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Porous Silicon (PS), thanks to its small thermal conductivity, is a promising candidate for future thermoelectric applications. Although the effect of morphological properties on thermal conductivity (e.g., porosity, pores' size, ...) has been largely investigated from both a theoretical and experimental perspective, a deep understanding of the microscopic vibrational mechanisms at the core of thermal transport in porous materials is presently necessary in order to properly manage the atomistic features for engineering applications.
In this study we perform an atomistic analysis of the vibrational properties of nano-porous silicon samples for different porosity levels through the calculation and diagonalization of the dynamical matrix. Following recent studies on amorphous materials [1,2], we propose a classification of the vibrational modes into extended and localized modes and calculate participation ratios, stretching factors and phase quotients.
We hence identify the *mobility edge* and argue that a definiton of the *Ioffe-Regel limit* (separating propagons from diffusons in amorphous materials) cannot usefully be applied to PS: for the values of porosity considered no frequency-resolved distinction between the two can be made. We then analyse the low-frequency behaviour of the vibrational density and discuss the modification in the frequency and amplitude of the boson peak.
Finally, we apply a modal analysis [3] to calculate the modal contributions to thermal conductivity and show how porosity induces 1) generally smaller thermal conductivity per mode on one side and 2) strong negative correlations among modes on the other. Hence, we show that these issues concur in the exponentially decreasing thermal conductivity of PS as a function of porosity.

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Figures

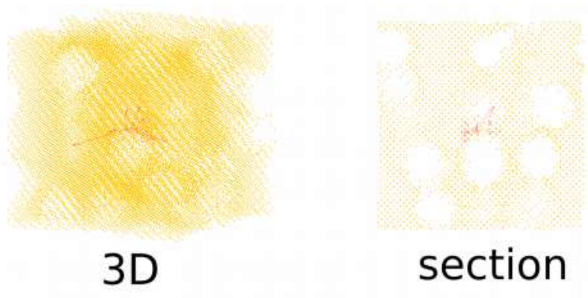

Figure 1: Atomic displacements (red arrows) in a localised mode in 30% porosity sample.

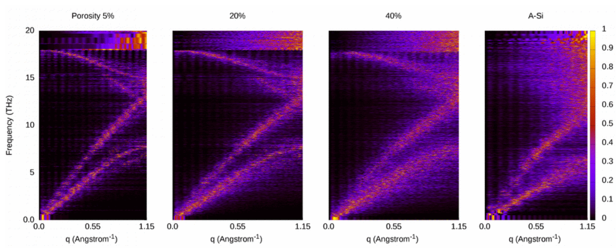

Figure 2: Dispersion curves of PS for increasing porosity whence the mobility edge and Ioffe-Regel limit are identified.

Multifunctional ceramic/graphene composites

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Abstract

Nowadays, advanced technological applications require the development of new multifunctional materials able to work under severe operating conditions. In this way, we have selected one of the most demanded engineering ceramics, in particular silicon carbide (SiC), to enhance their mechanical, damage resistance and tribological performances by incorporating graphene fillers into the ceramic matrix, also looking for new functionalities such as electrical transport. In this way, the developed dense SiC/graphene composites with up to 20 vol.% of graphene fillers were much more damage tolerant than the monolithic ceramics [1], reaching, at the same time, maximum fracture toughness and strength increments of up to 162% and 60%, respectively [2]. This better response is explained by the occurrence of crack shielding mechanisms promoted by the graphene sheets. Furthermore, graphene composites exhibited an enhanced wear resistance (70%) under dry sliding conditions [3] due to the formation of an adhered lubricating and protecting graphene-based tribofilm. Finally, the electrical conductivity increased with the graphene content up to three orders of magnitude, leading to a strong directional transport as well [4]. This better electrical response allowed electrical discharge machining SiC complex parts (Figure 1) [5].

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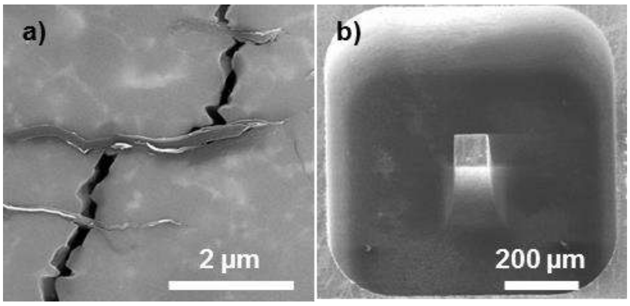

Figure 1: SEM micrographs of SiC/graphene composites showing: a) a crack shielded by graphene fillers and b) an electrical discharge machined micropillar.

New biocatalytic composites assembled by metal ion coordination

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We report a new protocol for the synthesis of organic/inorganic protein nanohybrids that leads to highly stable catalytic composites. Our approach is based on the combination of three advanced protein-stabilization techniques, i.e. the encapsulation via single enzyme polyacrylamide nanogels (SEN) [1], the confinement inside metal organic frameworks (MOFs) [2], and the embedment into organic/inorganic hybrid nanoflower structures [3]. Using SEN methodology [4-5], we are able to wrap individual enzymes with a porous polymer that is fully decorated with imidazole motifs. In presence of a divalent cation, such as zinc or copper, as it happens in MOFs, the nanogels aggregate driven by the imidazole-cation coordination and create nanoflower-like structures. Fabricated hybrids show higher activity and stability than other nanoflowers synthesized by previously reported protocols. Moreover, we were able to overcome common issues related to the performance of the biocatalyst: protein recovery (SENs are homogeneous catalysts), substrate transfer and diffusion to the cavity of the hybrids (main issue in protein-MOFs), and stability at low pH and the restriction to limited number of divalent cations (inorganic biomineralization of nanoflowers). Also, our approach allows to extend the nature of cations used so far for the biomineralization, including silver and gold salts. On top of it, this is the first report in which Ni and Cd protein nanoflowers are successfully fabricated.
Finally, this work highlights the significant potential for transition metal ion coordination as a tool for directing the assembly of hybrid materials.

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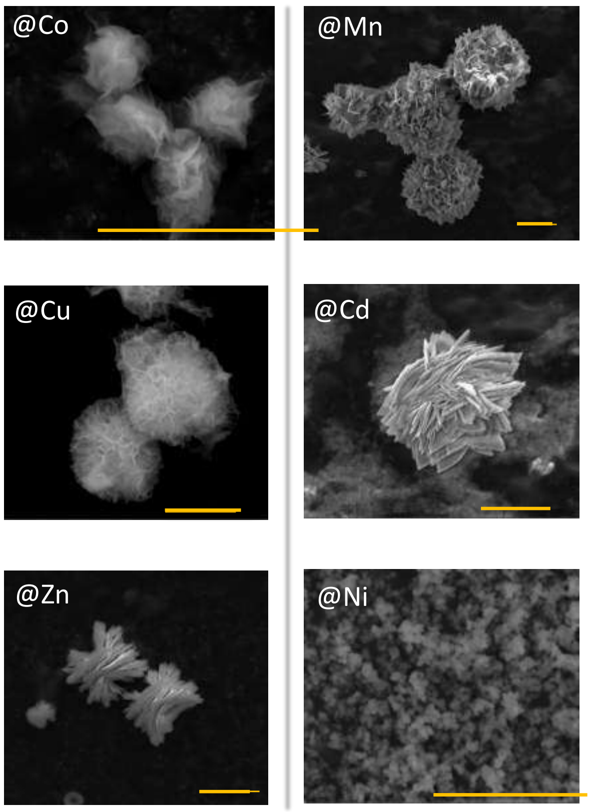

Figure 1: ESEM images of biocatalytic hybrids with peroxidase activity fabricated using an array of transition metal ions: Co(II), Mn(II), Cu(II), Cd(II), Zn(II), Ni(II). Bar: 5 µm

Synergic effect of magnetite nanoparticles and cellulose nanocrystals on shape-memory behaviour

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Abstract

Shape-memory polymers (SMP) are a kind of polymeric smart materials which stand out due to their ability to fix a temporary shape and recover their original shape as a response to an external stimulus. [1] Among SMP, segmented polyurethanes (STPU) are one of the most noteworthy because of their versatility. STPU are block copolymers formed by two blocks, the composed by a macrodiol and the formed by a diisocyanate and a low molecular weight chain extender.

According to economic, environmental and social concerns, the interest in the design of STPU derived from renewable sources is increasing. Therefore, in the last decade different biobased macrodiols, diisocyanates and chain extenders are employing in the synthesis of STPU. [1,2]

Moreover, shape-memory properties of STPU can be enhanced by loading different nanoentities. In addition, the incorporation of magnetic nanoparticles, such as magnetite nanoparticles (MNP), allows possibility to activate the shape recovery by applying a magnetic field, instead of heating up the sample. [3]

In this work thermo- and magneto-responsive biobased polyurethane bionanocomposites were prepared, loading different amounts of MNP, cellulose nanocrystals (CNC) and a combination of MNP and CNC (Figure 1). The effect of the nature and amount of the nanoentities on shape-memory properties was analysed.

Acknowledgements

Financial support from the Basque Government (IT-776-13). We also wish to acknowledge the "Macrobehavior-Mesostructure-Nanotechnology" SGIker unit from the University of the Basque Country, for their technical support. T.C-C. thanks the University of the Basque Country for DOKBERRI 2017 grant (DOCREC17/13).

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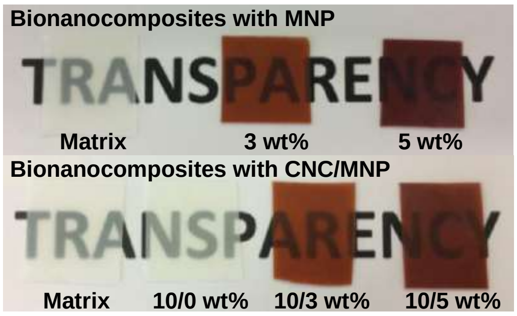

Figure 1: Digital images of the obtained polyurethane bionanocomposite films.

Silk fibroin/orange peel composite foam: an efficient adsorbent material for water remediation

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A novel highly porous adsorbent is prepared combining orange peel powder with silk fibroin, a biopolymer derived from Bombyx mori cocoons. Agricultural waste peels have been studied as promising bio-sorbents in water remediation for the removal of dyes and heavy metal ions due to their chemical composition[1], and the orange peel incorporation in the silk fibroin matrix allows to overcome the difficulties caused by the recovery of the ground sorbent during wastewater treatment. The carbon dioxide assisted critical point drying is used to fabricate a stable composite foam starting from alcogels obtained with the addition of methanol in order to induce the self-assembly of ordered β-sheet structures in the protein[2]. The successful embedding of 50%$_{w/w}$ of orange peel with respect to the silk fibroin has allowed the reaching of a maximum adsorption capacity of 113 mg/g for the model molecule methylene blue. The mechanism involved has been identified as a physical adsorption process. The use of orange peel as bio-sorbent introduces the possibility to valorize this agricultural peel waste and to reuse it to obtain sustainable adsorbent materials.

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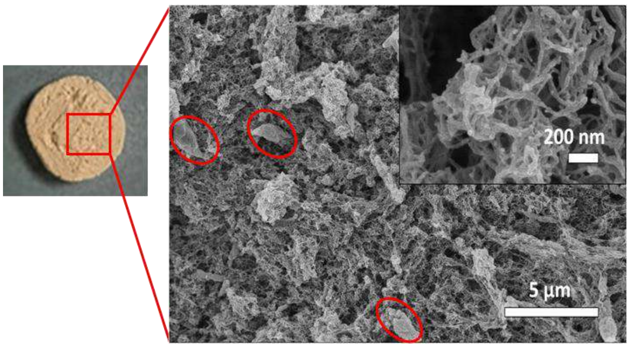

Figure 1: Picture and HR-SEM image of Silk Fibroin/Orange Peel foam. The presence of orange peel powder is indicated in the red circles

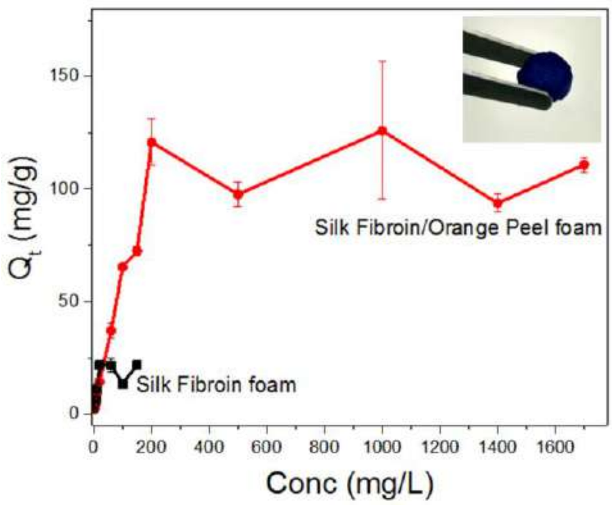

Figure 2: Effect of the initial methylene blue concentration on the adsorption capacity after a contact time of 24 h for the Silk Fibroin/Orange Peel and the Silk Fibroin foams

Sustainable long chain polyester bioplastics from tomato peel waste sources

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Tomato peels are an abundant raw material for multifunctional fatty acids. After peels' depolymerization using NaOH solutions, their chemical composition shows three main components: 10,16-dihydroxyhexadecanoic (43.2 wt.%), 9,12-octadecadienoic (16.1 wt.%), and 9-octadecenoic (11.9 wt.%) acids, respectively. Such monomers have been polymerized by a solvent-free melt-polycondensation method in the presence of $Sn(Oct)_2$, producing free-standing films. The conditions of the polycondensation were optimized in terms of temperature (150, 175, and 200°C), time of reaction (1, 3, 5, and 7 hours), and load of catalyst (0, 0.02, 0.05 and 0.1 mmol). The kinetic and thermodynamic parameters of the reaction were calculated by infrared spectroscopy (Figure 1a) of the resultant samples synthesized in the above conditions. Mechanical, hydrodynamic (Figure 1b) and thermal properties of free-standing films were related to the degree of polymerization and the amount of catalyst used for the polymer matrix synthesis.

Figure

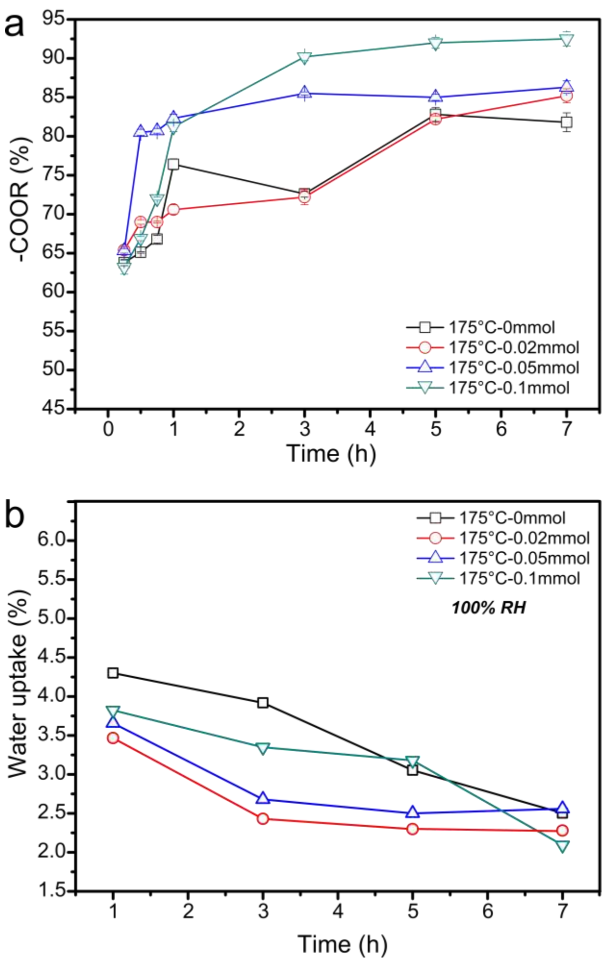

Figure 1: (a) Deconvolution of the carboxylate band using infrared spectroscopy and (b) Water uptake of the films in function of reaction time and catalyst concentration at 175°C, respectively.

Manufacture of electrically conductive PEEK filaments for 3D printing

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Electrically conductive composites based on high-performance polymers are interesting for use in, e.g., electrostatic dissipation, electrostatic painting, electromagnetic interference (EMI) shielding and lightning strike protection. A combination of high electrical conductivity, mechanical performance and service temperature is considered as particularly relevant for space applications. These requirements could be reached via the preparation of polymer nanocomposites containing suitable fillers. Carbon nanotubes (CNT) and graphite nanoplates (GnP) have excellent mechanical properties and high electrical conductivity. PEEK presents good mechanical properties, high thermal resistance and favours the interactions with those fillers.

The present work reports the manufacture by melt mixing of an electrically conductive composite containing PEEK, GnP and CNT, its processing into a continuous filament and its use in additive manufacturing. Challenges include attaining the required nanoparticle dispersion to achieve a conductive network (which is difficult due to the cohesiveness of the original particle agglomerates) together with good mechanical performance, good surface quality and dimensional precision.

Compositions and processing conditions yielding the higher electrical conductivities were selected. Then, filaments were obtained by twin screw extrusion and the effect of post-extrusion conditions was assessed. Finally, parts printed by Fusion Deposition Modelling (FDM) were characterized by tensile testing, electrical conductivity, and optical and electron microscopy

Figures

Figure 1: Extruder set-up

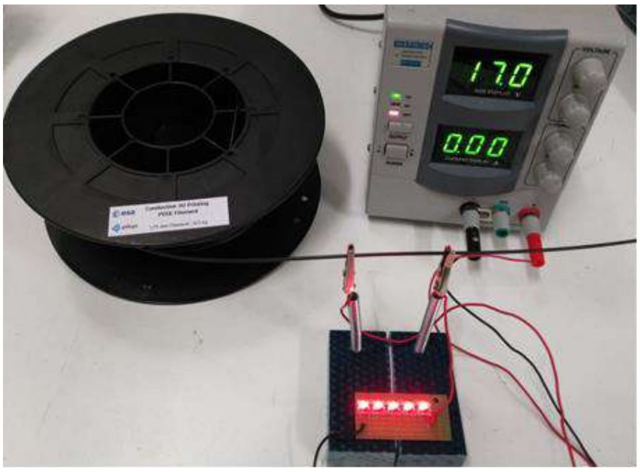

Figure 2: Conductive PEEK filament

Carbon fiber/graphene doped epoxy demonstrator for aeronautic applications

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The increasing demand of more efficient structures in terms of weight, cost and energy efficiency have gained a great importance in transport industry last years. This has resulted in the research of new multifunctional materials which fulfil these objectives. For this reason, the incorporation of graphene related materials (GRMs)to carbon fibre reinforced polymers (CFRP) is one of the solutions that are proposed to obtain multiscale materials that provide a multifunctional behaviour, opening new application fields that conventional composite cannot satisfy [1]. Several authors have confirm that the incorporation of GRMs to CFRP improve its performance [2,3].

In this work, carbon fiber/ graphene doped epoxy laminates with different lay-up and number of layers have been manufactured by hand-lay up. A complete characterization was carried out in order to evaluate the effect of graphene addition in mechanical, physic-chemical and electrical properties of CFRP. Afterwards, these materials were employed to manufacture an aeronautic demonstrator based on a skin with two stringers (Figure 1 and Figure 2).

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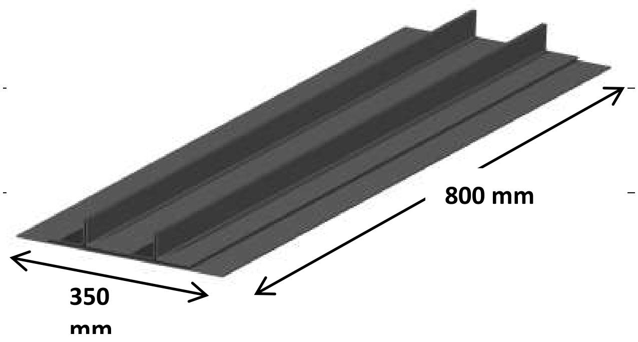

Figure 1: Final carbon fiber/graphene doped epoxy demonstrator

Smart nanomaterials with cellulosic matrix and magnetic properties

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Nanostructured cellulose availability is increasing in the global market. Several companies and research institutions are involved in the development and start-up of pilot to large scale production facilities, leading to an increase in a short-term production capacity [1]. Forecasts indicate that the largest consumption of this kind of materials will come from the paper, packaging and plastic industries, although the good value-for-money ratio indicates that other technical uses could be economically viable [2]. Magnetic materials are generally heavy, fragile and hard to processing, limiting their utilization in a wide range of potential applications. Smart papers are mainly composed by natural fibres that have been modified or enriched with additives, shifting the common use of paper towards new functionalities [3]. In this context, the development of smart materials based on nanostructured cellulose materials merges the excellent mechanical properties, and new "smart" properties, providing a significant added value to the product. By providing magnetic properties to paper-like produced sheets or films, a wide number of possible applications have been reported [4]. The main aim of this work is to obtain a nanocomposite preserving the inherent properties of the cellulose or nanostructured cellulose paper and increase the added value of the material with magnetic properties. From OCC pulp as raw material, we have explored two nanocomposite obtaining methods. Characterization of nanoparticles and fibres, physical, mechanical and new magnetic properties of paper will be analyzed and discussed.

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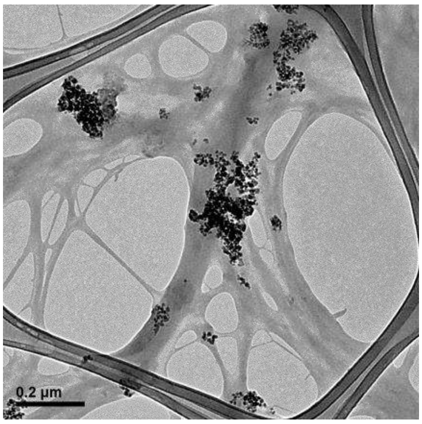

Figure 1: TEM image of magnetic nanoparticles attached to OCC nanofibrillated cellulose.

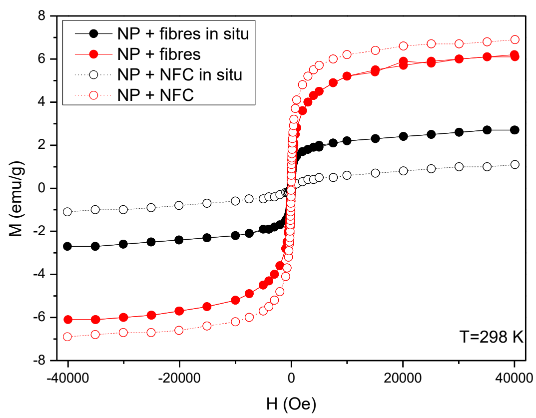

Figure 2: Isothermal magnetic behaviour of nanocomposites

Starch based 'click' cross-linked conductive nanocomposite hydrogels

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In this work, a friendly strategy was proposed to obtain starch based conductive hydrogels. Cross-linked hydrogels were obtained by aqueous Diels-Alder (DA) reaction of furan-modified starch and a bismaleimide. Graphene was incorporated as conductive nanofiller using natural surfactants to improve its stability in water.

Firstly, starch was functionalized with furan moieties by the reaction of gelatinized starch with furfuryl isocyanate. Then, hydrogels were obtained through DA reaction using a water soluble bismaleimide [1]. The influence of using different Fu:Mal weight ratios was investigated.

The effectiveness of the DA reaction to form the hydrogels was studied by FTIR and UV-spectroscopy. Besides, it was founded that the use of different Fu:Mal weight ratios resulted in differences in the rheological behaviour, morphology and swelling capacity of the hydrogels. The highest Fu:Mal weight ratio was selected for the nanocomposite hydrogels since it showed the highest storage modulus and interesting interconnected porous structure.

Hence, conductive nanocomposite hydrogels were carried out by adding graphene [2] as nanofiller previously dispersed in water using surfactants from natural sources.

Upon the addition of graphene the hydrogel showed improved viscoelastic behaviour and presented antimicrobial activity against *E. coli* and *S. aureus*. Regarding to the electrical conductivity, it was significantly increased for the graphene containing sample.

Acknowledgment

Financial support from the Basque Country Government in the frame of Grupos Consolidados (IT-776-13) is gratefully acknowledged. Technical and human support provided by SGIker (UPV/EHU, MINECO, GV/EJ, ERDF and ESF) is also gratefully acknowledged. K. González thanks the University of the Basque Country for the PhD grant (PIF-G-003-2015).

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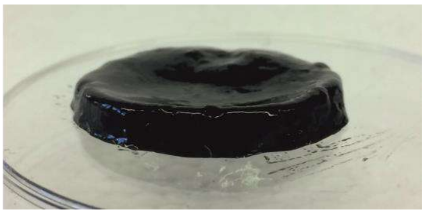

Figure 1: Obtained starch based conductive nanocomposite hydrogel.

All natural bioplastics from cellulose and cellulose-rich agro-wastes

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Since the middle of the 20th century, the need of functional and low-cost materials for the production of commodities for the growing population of our planet has led to a rapid development of the petroleum-based plastics industry. In fact, plastics prepared from fossil resources are everywhere. Nevertheless, the massive use of these materials is associated with numerous environmental problems (pollution, sorting, recycling, and greenhouse effects). As a realistic alternative, bioplastics, this is, plastics made from renewable raw materials have been developed.

In this work, we present a simple and direct method to produce bioplastics from cellulose and cellulose-rich materials from both terrestrial and aquatic plant wastes. In particular, we report the preparation of bioplastics from cellulose-rich plant residues such as parsley, cocoa or seaweeds, to mention a few, blended with cellulose using trifluoroacetic acid (TFA) as a common solvent [1-3]. Chemical, morphological and structural characterization was performed for all the films. Mechanical and hydrodynamic properties were also investigated, showing a wide range of results, Figure 1. Moreover, biodegradation tests were carried out, indicating that the films degrade completely in seawater, Figure 2. Finally, some bioplastics were characterized by a good compatibility, high antioxidant properties and an anti-inflammatory activity similar to commercial drugs. Hence, these bioplastics could be used in different applications such as food packaging or biomedicine.

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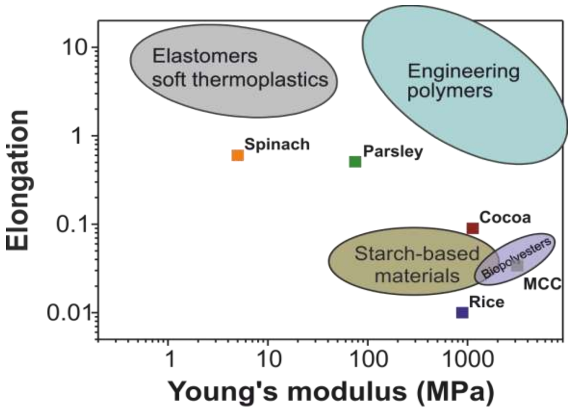

Figure 1: Mechanical comparison between bioplastics from plant wastes and commercial plastics.

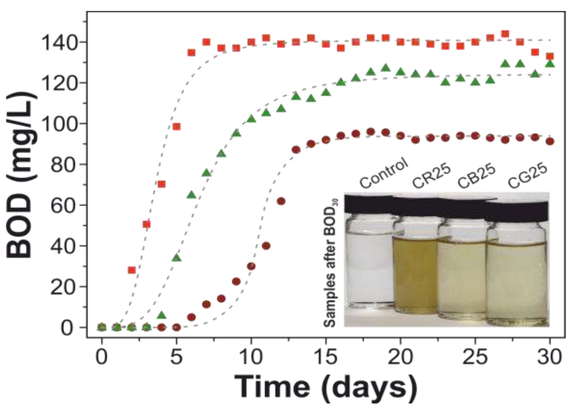

Figure 2: Biological oxygen demand of bioplastics prepared from seaweeds.

Fabrication and characterisation of Ion conductive polymer - graphene nanoplatelets composite thin films

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Abstract

Polymer-Graphene Nanoplatelets (P-GNPs) nanocomposite dispersion was synthesised using two different types of conductive polymers: cation and anion. The nanocomposite was utilized to fabricate thin films by two methods. The Langmuir-Schaefer (LS) technique has been used for the synthesis of ultra-thin films of the nanocomposite in different substrates such as Silicon oxide, glass, glassy carbon electrode and Indium tin oxide [1]. Brewster Angle Microscopy was utilised to investigate the Langmuir monolayer formation at the air-water interface. The commercial synthesis of thin films was analysed using the Layer by Layer method. The morphology and thickness of the films were studied using SEM, White Light Interferometer, Raman and optical microscopies. The films were used for the electrochemical detection of different analytes such us Vitamin C [2], Dopamine, Caffeine, Nitrites and THC (Tetrahydrocannabinol)[3].

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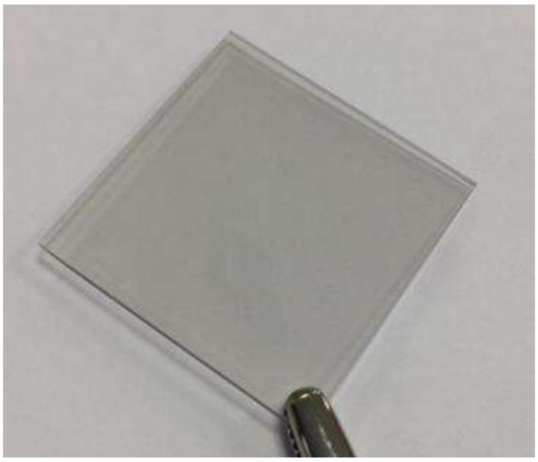

Figure 1: *10 ultra-thin layers of Nafion- Graphene Nanoplatelets nanocomposite in Indium Tin Oxide (ITO) substrate; using the LS as a synthesis method.*

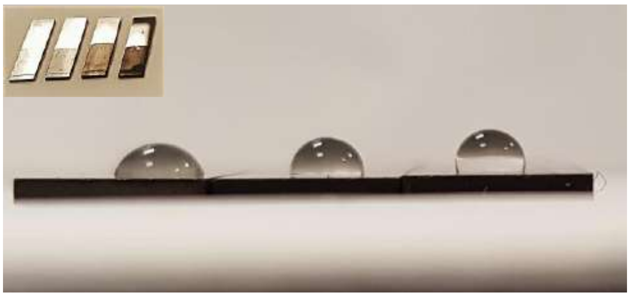

Figure 2: Different thickness of polymer graphene nanoplatelets films in glassy carbon electrode substrate (GCE). DI water has been dropped on the surface to prove the increase of the thickness using the Layer by Layer method. The inset photo corresponds to 2, 5, 10 and 20 layers of the nanocomposite, where the increase of the thickness is visual.

Effect of different types of electrospun polyamide 6 nanofibres on the mechanical properties of a carbon fibre/epoxy composites

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Abstract

Delamination and brittle matrix fracture has since long been a problem of fibre reinforced composites. Recently, the incorporation of nanofibre veils has been shown as an effective method for improving mechanical properties of these composites, without causing problems during impregnation and without negatively affecting other properties [1], [2]. These nanofibers thus have potential to serve as through-the-thickness reinforcing agents in woven composites. The effect of electrospun nanofibrous veils made of two different type of polyamide 6 on the mechanical properties of carbon fibre/epoxy composites has been investigated. The nanofibres were incorporated in the carbon fibre/epoxy composite as stand-alone interlayered structure. Incorporation of polyamide increases the mechanical properties of the composites. For composites with one PA6 nanofibre veil in the middle thickness position of the composites, between the carbon fibre plies, the stress at failure during the flexural mechanical tests increases between a 19 % and 42 % as a function of the physico-mechanical properties of the PA6 employed in the veils preparation. The analysis of the fracture indicates that the veil hinders the crack propagation in the composites. Furthermore, G_{IC} value increases between 20 and 44 % for composites modified with a veil of the different PA6 employed. This increment is due to the crack propagation across the PA6 veil, which result in a high energy absorption of the veil.

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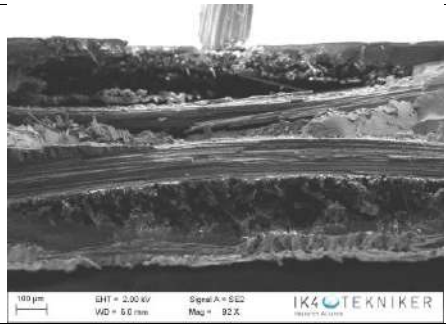

Figure 1: SEM of the composite with a veil of PA6 Ultramid

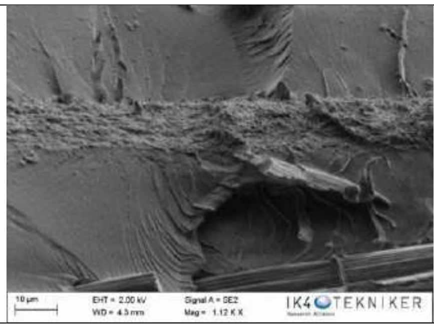

Figure 2: SEM of the veil of PA6 Ultramid within the composite

Microstructure and mechanical characterization of thin bioactive PEO coatings fabricated on UFG CP Ti

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Abstract

Plasma Electrolytic Oxidation (PEO) coatings were deposited on Ultra-Fine Grained Commercially Pure Ti (UFG CP Ti). The objective of the deposited coatings is to provide enhanced bioactivity to the protective anodic TiO_2 film by the incorporation of Ca and P ions. Three coatings were deposited under the same processing conditions using three electrolytes containing Ca and P species with different pH levels. All the deposited coatings were characterized by a high surface roughness and high porosity. Nanopores and random-shape micro-cavities were found through their thickness. However, the surface and through-thickness morphologies developed were different from one coating to another. The composition and the phases present were also evaluated by means of EDX and XRD, respectively. The presence and the amount of Ca and P elements depended on the electrolyte. Nanocrystalline TiO_2 anatase and rutile phases were found, being Anatase the predominant phase in all the coatings. The sample corresponding to the lowest pH electrolyte did not present the rutile phase. In the other two samples, rutile had a significant presence in one of the samples while in the other one its contribution was minimal. The mechanical characterization of the coatings was carried out by nanoindentation. This represents a challenge, due to the inherent porosity and large roughness characteristic of PEO coatings. To overcome this challenge, low-depth nanoindentations (~150 nm) were performed on the cross-section of the coatings, and care was taken to minimize the influence of micro-cavities. The correlations between the mechanical properties and the phase composition of the coatings will be presented.

Figures

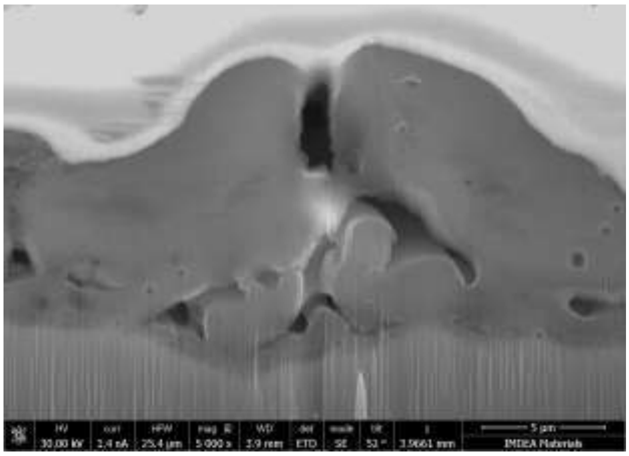

Figure 1: Cross-section of a PEO coating obtained by Focused Ion Beam milling. Thickness between 10-15 µm.

Figure 2: Bright field TEM image of a PEO coating. The figure shows coexistence of both nanocrystalline titania and amorphous Ca/P containing domains

The potential of graphene oxide and reduced graphene oxide in fabrication of 3D printed ceramicand polymeric composites

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Graphene, a monolayer of carbon atoms arranged in a honeycomb lattice, has shown impressive thermal, mechanical, and electrical properties, and is a promising alternative as a reinforcement to tailor the material structure at nanometre scale in order to obtain stronger and tougher engineering composites.

Additive manufacturing method (AMM), has opened new doors for fabricating 3D composites with complex shapes. Robocasting and Fused deposition Modelling (FDM) are examples of commonly used AMMs[1].

The current Work reports the use of graphene-like nanoplatelets to enhance the mechanical performance of scaffolds made of ceramics and polymers matrices, fabricated by robocasting and FDM, respectively. These composites have a wide range of application including high wear components, nuclear reactors, light-weight armor and biomedicine. According to our results, it was found that the addition of GO platelets up to 2 vol.% content enhanced the mechanical performance of the ceramic scaffolds in terms of strength and specially toughness. Moreover, addition of 5 vol. % to polymeric matrix resulted in 80% improvement in the compressive strength.

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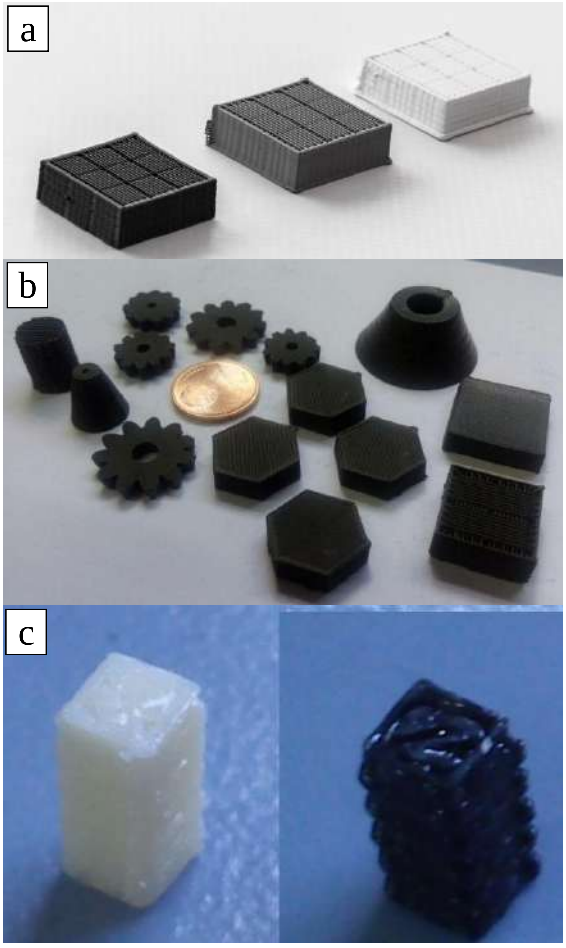

Figure 1: Optical images of 3D porous and dense scaffolds produced by robocasting. (a) Bioglass/rGO composites. (b) B4C/rGO with different shapes and (c) PLA and PLA/rGO scaffolds printed by FDM. The difference in the color is due to presence of rGO in the structures.

Sustainable fabrication of hydrophobic composite films inspired by plant cuticles

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Abstract

Plant cuticles are the outermost membranes that cover and protect the aerial organs of plants [1]. Cuticles are mainly composed by polysaccharides, cutin, and waxes. Cutin is the main component of plant cuticles, being the polymer matrix that supports the rest of the cuticle components [2]. Cutin of tomato fruits is mainly composed by hydroxylated fatty acids. In this work, tomato cutin monomers (C) were dissolved in ethanol through a sonication process and blended with an aqueous solution of sodium alginate (A). Different alginate/cutin weight ratios (100/0, 75/25 and 50/50) were prepared. Free-standing films were obtained and characterized to study morphological, mechanical, thermal, hydrodynamic and barrier properties. In addition, to induce the esterification of cutin monomers, all the materials were heated in oven at 150°C for 8 hours. A/C 50/50 sample resulted the best composite material with an interesting morphology and hydrophobic behaviour. Nevertheless, to enhance its mechanical and barrier properties, three different percentages (5, 15, 30 wt.%) of beeswax (BW) were added. The addition of beeswax led to a significative increase of both mechanical and water barrier properties. These green alginate-cutin-beeswax composite materials could be potentially used in food packaging.

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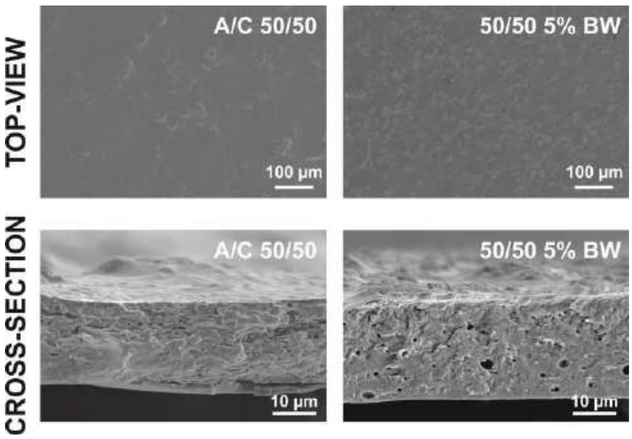

Figure 1: SEM top-view and cross-section images of A/C 50/50 sample after heating treatment and after addition of 5 wt.% beeswax (A/C 50/50 5% BW).

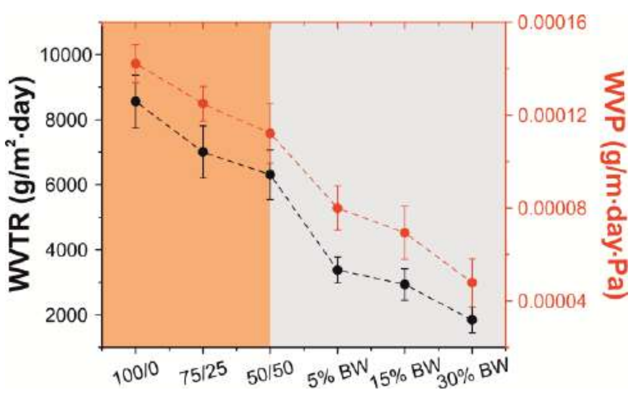

Figure 2: Water vapor transmission rate (WTR, black) and water vapor permeability (WVP, red) of alginate/cutin polyester after heating treatment (100/0, 75/25, 50/50) and after addition of beeswax (5% BW, 15% BW, 30% BW).

COMPOSITES2018 – POSTERS

Modification of graphene with ionic liquid to reduce the electrical percolation threshold in bio-based TPU nanocomposites

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During the last years, the development of polymeric materials obtained from renewable resources have become one of the most interesting research fields due to environmental and economical issues [1]. Bio-based thermoplastic polyurethanes (bTPU) are one example of these kinds of bio-based polymers that are already commercially available.

Several properties of these bio-materials, including mechanical, thermal or electrical properties, can be improved by the addition of nanofillers, such as graphene, obtaining high-performance nanocomposites (NCs). However, one of the main drawbacks when attempting to effectively disperse nanofillers in the polymeric matrix, is their tendency to re-aggregate [2]. As a consequence, the electrical percolation threshold is usually rather high and the extent of mechanical properties' improvement limited.

In this work, bTPU/graphene NCs were obtained by melt mixing. In order to reduce the re-aggregation of neat graphene during processing, it was previously modified with an ionic liquid. The NCs were obtained by extrusion and the standard test specimens were obtained by injection and compression moulding. The phase structure, the nanostructure and the electrical and mechanical properties were characterized and compared.

The modification of the graphene with the ionic liquid caused an improved dispersion that led, in turn, to a significantly lower electrical percolation threshold (Figure 1). However, the Young's modulus of the NCs was not affected because the positive effect produced by the improved dispersion was counteracted by the negative effect provoked by ionic liquid (Figure 2).

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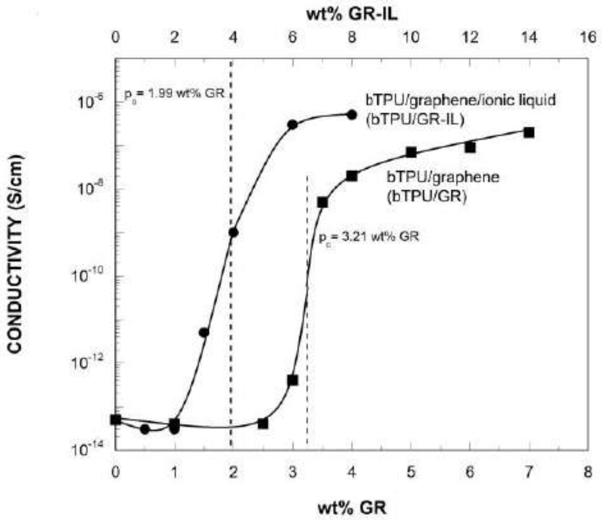

Figure 1: Electrical conductivity of bTPU/GR-IL (●) and bTPU/GR (■) NCs, as a function of both GR and GR-IL contents.

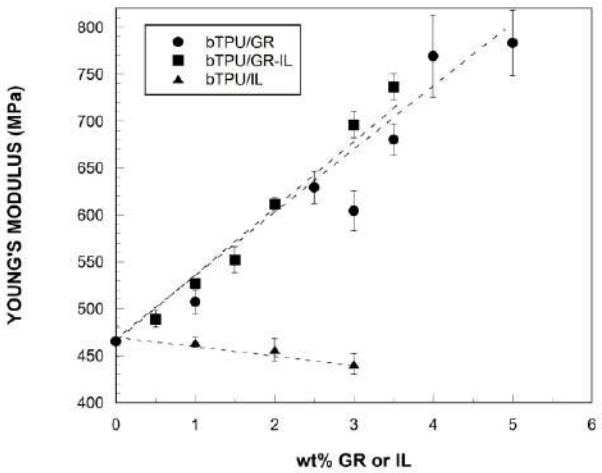

Figure 2: Young's modulus of bTPU/GR and bTPU/GR-IL NCs and bTPU/IL blends.

Mechanical Properties of Gelatin Reinforced with Nanocellulose

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Organic rodlike cellulose nanocrystals extracted from sisal fibers and inorganic montmorillonite based on silicate layers were employed to develop bionanocomposites based on gelatin matrix. Bionanocomposites with cellulose nanocrystal, montmorillonite and both nanoreinforcements combined were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry.
Tensile properties values were determined to study the influence of the addition of nanoreinforcements, different in nature, to gelatin matrix. Bionanocomposites with montmorillonite improved tensile strength but systems reinforced with nanocellulose showed lower tensile strength than neat gelatin ones.

Acknowledgments
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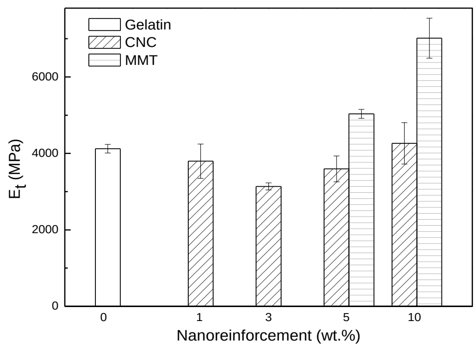

Figure 1: Tensile modulus of composites.

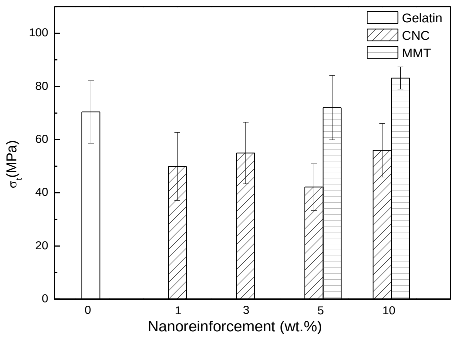

Figure 2: Tensile modulus of composites.

Intragranular reinforcement of alumina-based composites with carbon nanotubes via sol-gel

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The reinforcement of the ceramic matrix composites has been widely studied by the inclusion of carbon nanotubes (CNT) [1]. Nevertheless, the efficiency of this reinforcement when the CNT are located in the grain boundaries is still under debate. In this work, the synthesis of the composites has been designed with the aim of achieving an intragranular presence of the CNT in order to reach a more efficient reinforcement.
Different routes based on the sol-gel method were tested to prepare alumina based composites with CNT [2,3]. The CNT were mixed by the addition of a basic suspension of CNT upon high power ultrasounds. The pH and ultrasounds enhanced the good dispersion and disentanglement of the CNT, but they also contributed to the rapid and controlled gelation of the samples. Finally, alumina composite powders were submitted to Spark Plasma Sintering. First CNT contents covered a range from 0.00 to 1.00 wt.%.
The obtained alumina gels showed good homogeneity at optical level, and no coils or agglomerates of CNT were observed by electron microscopy (SEM). In addition, images showed the presence of the CNT within the core of the particles of the gel (Fig. 1).
Mechanical properties were assessed by indentation techniques. First results (Fig. 2) showed relevant reinforcements, such as a two-fold increase in Vickers hardness (HV) with the addition of 0.50 wt.% of CNT. These findings confirm the sol-gel route as a promising strategy for fabricating ceramic reinforced with carbon nanotubes.
Project P12-FQM-1079 and funding support to TEP115 and FQM163 from Junta de Andalucía, Acc.Esp.IV.11-180000999 and V M-F's grant from Plan Propio Inv. (Universidad de Sevilla) are acknowledged.

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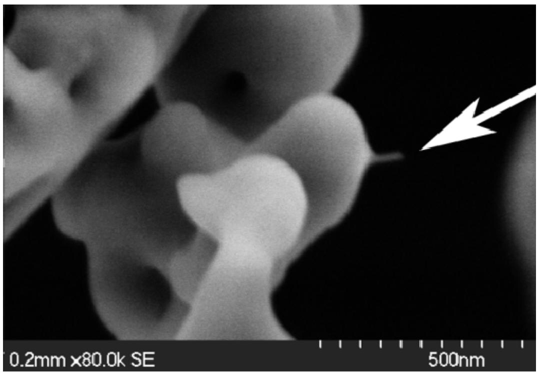

Figure 1: SEM picture showing one CNT (arrow) within alumina particle, prior to sintering

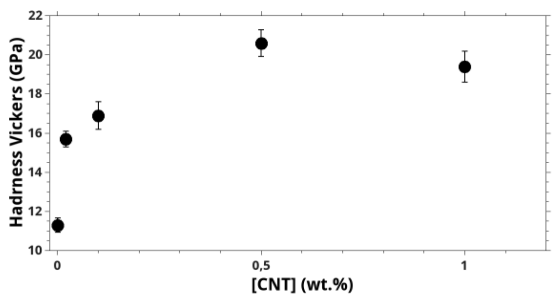

Figure 2: HV with 10 kp load for alumina samples with 0.00, 0.05, 0.10, 0.50 and 1.00 wt.% of CNT

Office Waste Paper as Cellulose Nanocrystal Source

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Cellulose nanocrystals (CNC) were isolated from office waste paper using an alkali solution treatment and a subsequent acid hydrolysis process with 64 wt% H_2SO_4 at 45 °C for 30 min [1]. The CNC obtained after 2 wt% NaOH treatment and the subsequent acid hydrolysis was labelled as CNC1, while the CNC obtained after 7.5 wt% NaOH treatment was labelled as CNC2. Figure 1 shows the X-ray diffractograms of office waste paper and CNCs. All diffractograms showed peaks related to cellulose I [1,2]. Nevertheless, CNC2 sample showed peaks related to cellulose II [1,3] suggesting the partial conversion of cellulose I into cellulose II. Moreover, diffractograms of office waste paper showed peaks related to calcite [1,4] whereas in the diffractograms of CNCs, these peaks were not observed corroborating the removal of calcite. Figure 2 shows the micrographs obtained by atomic force microscopy (AFM). AFM micrographs confirmed the presence of cellulose nanocrystals and it was observed that the diameter of CNC samples was around 5-6 nm and the length of isolated CNC samples varied with the applied alkali treatment.

Acknowledgments
Authors are grateful for the financial support from the Basque Country Government in the frame of Consolidated Groups (IT-776-13) project. Authors also thank for technical and human support provided by SGIker of UPV/EHU and European Funding (ERDF and ESF).

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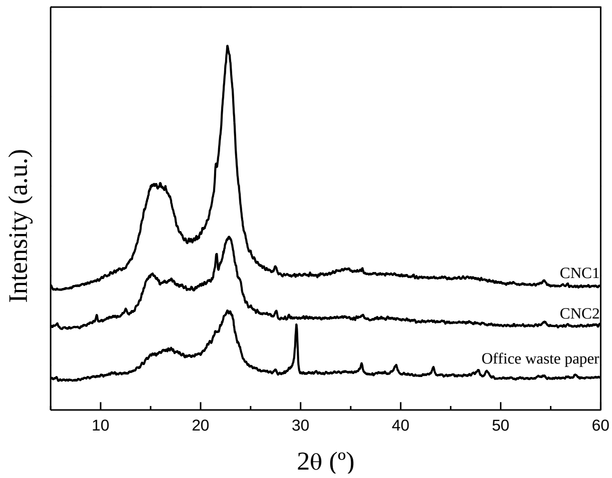

Figure 1: X-ray diffractograms of office waste paper and CNCs.

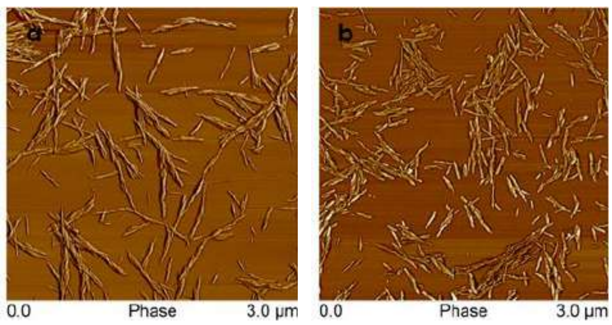

Figure 2: AFM of CNC samples obtained after different chemical treatment conditions: (a) CNC1 and (b) CNC2.

Monolithic homogeneous silica-graphene oxide aerogels synthesised via pH-controlled rapid gelation

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Silica aerogels have been considered for a variety of applications, such as thermal insulation, gas sensors, or biomaterials, thanks to the versatility of the synthesis procedure. Very recently, graphene is being embedded into silica aerogels broadening the possible functionalities of these materials [1-3]. This work introduces a rapid controlled gelation synthesis procedure for obtaining monolithic graphene oxide (GO) – silica aerogel composites, and describes their structural and mechanical properties.

Samples from 0.0 to 4.0 wt.% of GO were obtained by a pH-controlled rapid gelation route that enables the GO to be "frozen" homogeneously dispersed into the highly porous silica matrix, almost instantaneously. Sol is created by mixing a GO suspension in absolute ethanol, acidic water and TEOS upon sonication. Next, basic water is added while pH is controlled. After that, gelation takes place in less than 45 s, and finally, aerogels were obtained via supercritical drying in ethanol. Obtained aerogels after supercritical drying can be seen in Figure 1.

Densities of the sample series were almost constant, ca. 80 mg/cm^3 in all cases. N_2-physisorption show that the S_{BET} is almost doubled, from 490 m^2/g (pure silica sample) to 900 m^2/g (4.00 wt.% GO). SEM imaging revealed that the morphology of SiO_2 matrix based on the aggregation of spherical particles (~50 nm size) is maintained, even with the incorporation of high content of GO. Raman analyses confirmed that the difference between the characteristic peaks of SiO_2, (2896 and 2936 cm^{-1}) decreased with GO content thus, confirming hybridization of SiO_2 with GO.

Uniaxial compression tests reveal that compressive strength and maximum deformation decrease by the inclusion of 1.00 wt.% GO. Nevertheless, higher GO contents lead to an increasing trend and 4.00 wt.% composite presents similar properties than the pure silica sample (140 ± 40 kPa and 38 ± 4%). Higher mechanical values can be expected for higher GO contents. Besides, Young's modulus exhibits a reduction from 330 ± 30 kPa for pure silica sample to 295 ± 7 kPa, for the 4.0 wt.%.

The rapid controlled gelation is confirmed as a promising procedure that will enable further research lines for new technological applications for silica-graphene hybrid composites.

Projects PI-0013_2017_ITI, 2017-00001060, GRAMOFON-727619;H2020-LCE-24-2016, V.M-F's, J.A.D-F's grants (PPITUS) and M.V.R-P's "Contr. personal apoyo I+D+I 2017" (Andalucía, Spain) are ackowledged. Graphene oxide supplied by Graphenea.

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Figure

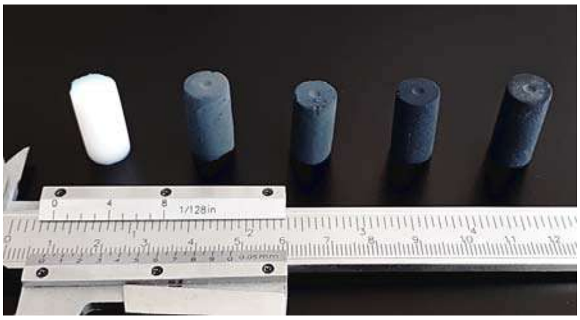

Figure 1: From left to right, monolithic hybrid aerogels with GO contents ranging 0-4 %wt.

Multifunctional nanocoating: hydrophobic and wear resistant properties

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Usually hydrophobic surfaces present a very limited mechanical wear robustness and long-term durability [1]. It has reduced their utilization in industrial applications where both requirements are needed, as building elements outdoor. Existing a large number of works about hydrophobic coating developments [2,3,4], but in them it is not assessed the hydrophobicity when the coating surface is subjected to wear processes. On the other hand, in the literature there are works about wear resistant coatings, but they do not provide hydrophobic performance [5]. The aim of this work has been to develop of transparent nanocoating with hydrophobic and wear resistant properties simultaneously. It is based on functionalisated SiO2 nanoparticles. It has been applied and evaluated on mortar specimens, through hydrophobic and wear testing. It is proven its hydrophobic/superhydrophobic character and enhanced wear behaviour.

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Figures

Figure 1: Superhydrophobic behaviour (CA above 160°) of the developed transparent nanocoating applied on mortar specimen, after 40 cycles of abrasion test.

INDUSTRIAL FORUM – SPEAKERS

Nanotechnology in medicine: risk assessment

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Currently there are approximately one hundred nanotechnological products applicable in nanomedicine and available in the market. The common known engineered nanomaterials when applied in medicine are also known as **NanoBioMaterials** (NBM). They can be differentiated into metals or metal oxides, of ceramic origin, other hybrids, those based on carbon, or of organic origin. Depending on their bioreactivity grade, NBMs can be classified in bioinert, bioactive, biomimetic, bioresorbable, or stimulating specific cellular responses at molecular level.

They are used as treatment in therapies against cancer, hepatitis and infectious diseases; as anesthetics, for the treatment of cardiovascular problems, in disorders inflammatory and immunological; in pathologies endocrine diseases, in degenerative diseases and in many other cases.[1] [2] Nanomedicine also raises large challenges when facing problems of health through the development of novel diagnostic methods, the improvements in the administration systems of drugs, effective tools for monitoring of the biological parameters, devices which allow the elimination of pathogens microorganisms, artificial cells and mechanisms that make immunological rejection impossible in organ transplants, leaving behind this way a lot of the strategies used by conventional medicine, nowadays very useful for vaccine development and applications.[3]

However, there are still several hindrances in the use of NBM related to their safety, considering that NBM present practically the same potential routes of exposure as another pollutant: dermal, respiratory or oral. Studies reveals various ranges of toxicity and biocompatibility, which reflects the distinct response of biological system toward different nanostructures and nanomaterials. To date, the knowledge on the interactions of nanomaterials with biological systems is limited and harmonized standards do not exist.

In this sense, it is important that the risk assessment considers not only the use in the consumer, but the entire life cycle of the product. Life Cycle Assessment (LCA) and environmental risk analysis (RA) are both suitable methods to assess the environmental and safety performance of a product. But in the NBMs case, The LCA studies existing thus far in nanotechnology have barely begun to cover aspects related to robust data collection or the degree of detail on the level of nanoparticle emissions[4], so it is necessary to increase the knowledge in this field.

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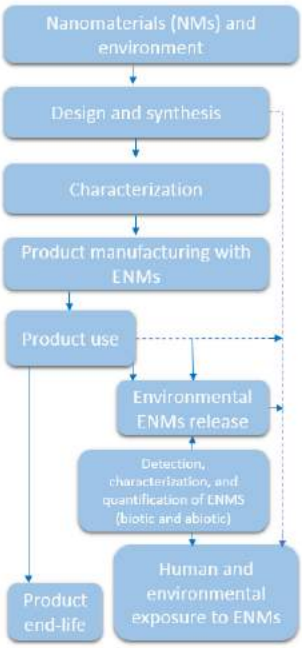

Figure 1: Main lyfe cycle stages of an engineered nanomaterial extrapolated to a nanobiomaterial

Supporting internationalization of Spanish companies through technological cooperation

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The international R&D&i projects headed by companies, at both multilateral (Eureka and Iberoeka) and bilateral levels, refer to the value added of innovation performed internationally and enable Spanish companies to reinforce their technological capacities, simultaneously expanding the impact of their products, processes and services on global markets.
An Impact Assessment[1] carried out during the Spanish Eureka Chairmanship[2] (July 16-June 17) shows a positive effect of the international R&D&I projects on the companies involved: one year after the end of projects, participants showed and additional annual turnover growth of 15% and an additional annual employment growth of 4% (network projects) 7% (cluster projects) compared to non-participating firms.

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[2] http://www.eurekanetwork.org/content/spanish-chair-final-report

Figures

Figure 1: Geographical distribution of CDTI´s Foreign Technological Action

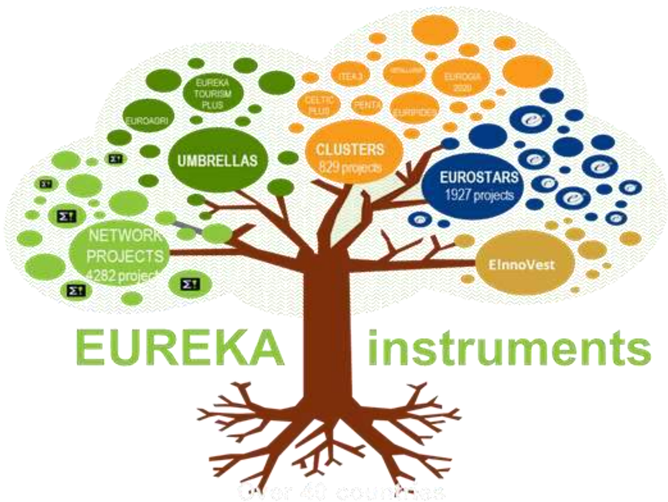

Figure 2: EUREKA Instruments

Electron beam lithography: spintronics and nano-optics applications

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I will discuss several examples of nanodevices fabricated by electron beam lithography (eBL) at CIC nanoGUNE. These nanostructures are employed for different research topics and applications in the fields of spintronics and nano-optics.

As example of spintronics devices I will introduce the lateral spin valve and its use as a spin-to-charge current converter [1,2] or a spin field-effect transistor (Fig. 1) [3].

As example of nanooptics devices, I will explain graphene-based plasmonic devices such as resonant metal antennas on graphene (Fig. 2) [4] and graphene nanoresonators [5], as well as hexagonal boron nitride-based phononic devices such as waveguide nanoantennas [6].

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Figures

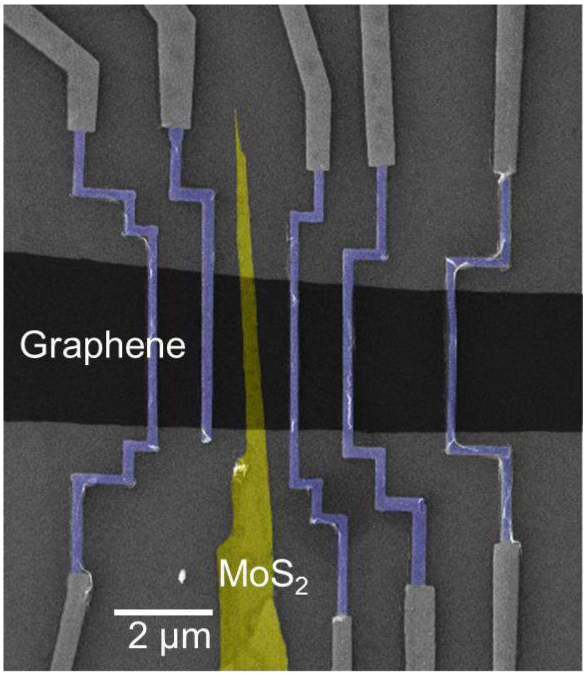

Figure 1: False-coloured SEM image of the 2D van der Waals heterostructure to be used as spin field-effect transistor. Purple nanostructures are Co electrodes fabricated by eBL.

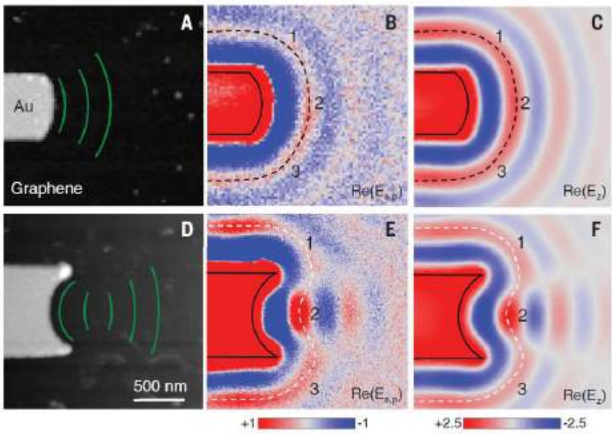

Figure 2: Convex (A) and concave (D) Au antenna on top of graphene fabricated by eBL. (B) and (E) are the corresponding experimental near-field images Re($E_{s,p}$). (C) and (F) are the calculated near-field images Re(E_z).

The Scaling of Reproducible Graphene for Industry Use

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Over the last few years, Graphenea has invested in expanding its team, facility and production capacity of both the Graphene Oxide and CVD Graphene Films to supply the needs of the growing graphene market. By making these strategic investments and developing a clear roadmap for both GO and CVD graphene, Graphenea has been able to keep pace with the demand of the graphene market. Ultimately, the key to success will come from working hand in hand with our industry partners to achieve their research milestones.

“Graphene and 2D Materials” EUREKA Cluster: Fostering European Competitiveness

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The “Graphene & 2D Materials” EUREKA cluster is defined as a complementary enabling and accelerator instrument in the European scene, fully piloted by industries to further take graphene from the mature research developed at academic laboratories into the European society in the space of 5 years, boosting economic growth, jobs creation and international leadership and investment attractiveness. This cluster will help Europe having a more dominant position in graphene patenting, will deploy the proper winning industrial strategies to gain worldwide competitiveness, and will ensure that for all promising industrial sectors of technology innovation, a fully integrated EU-value chain is established, integrating into consortia the relevant actors from low to high Technology Readiness Levels (TRL).

The cluster will clarify the differentiating potential in all sectors where EU-industries is strong and could further gain in competitiveness and will develop proper incentives towards the achievement of EU-leadership in the fields of graphene commercialization and graphene-driven technology improvement. The cluster will elaborate and foster industrially-driven innovation strategies, that will take advantage of the existing excellent science and transnational platforms in Europe (national networks, Graphene-Flagship, etc.), and will focus on solving current challenges which are limiting the time to market and business growth of graphene-related EU companies.

Graphene has a huge potential to impact established industrial sectors, building new emerging industries and niche segments and creating economic value. The “Graphene and 2D Materials” Strategic Research Agenda currently targets 7 interlinked priority R&D areas for Europe. These areas are (1) Standardization, (2) Production and Scalability, (3) Composites, (4) Energy, (5) Biosensors and Health, (6) Optoelectronics and Electronic Devices; (7) Functional coatings. Currently, 243 Institutions from 27 countries (among them 154 companies) expressed interest in joining the Cluster...

Collection of data and monitoring the efficacy of Risk Mitigation Measures in caLIBRAte

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Abstract

Various EU funded Projects have developed predictive Models and Tools to assess potential risks associated to nanotechnology.

caLIBRAte project main goal is to funnel the state-of-the-art in nanosafety research and merge it with state-of-the-art risk governance and communication sciences to establish a versatile risk governance framework for assessment and management of human and environmental risks of NM and NM-enabled products. The ultimate goal is that the quality and trust in the nano-specific models in the caLIBRAte risk governance framework will exceed current level of most existing REACH tools.

One of the main tasks in calibrate is to gather (and generate) high quality data, including data on Value-Chain Case-Studies. Data belonging to concluded and ongoing EU Projects was inventoried, and the associated datasets evaluated for their quality and completeness.

Additionally, new case studies will be generated to provide high quality data for model calibration and validation selected for caLIBRAte framework. One of the new case study focus on a nano-based paint that will allow collection of data in all the stages of the value chain. The measurement campaign associated to this case study will allow the identification of potential risks and the eventual need to adopt some Risk Mitigation Measures (RMM).

In this presentation, the strategy for collecting and compiling data in an organized way will be described, as well as the experimental setup to collect and generate data will be shown for the nano-based paint case study.

Graphene & 2D Materials Cluster: Funding Projects in Spain

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R&D International Cooperation Projects: promoted by international consortia related to Spanish participation in international technological cooperation programs managed by CDTI such as Eureka Graphene & 2D Materials Cluster, the project funding method for Spanish companies could be:

- Partially Reimbursable Loan, up to a maximum of 75% of the approved total budget, with a stretch of non-refundable up to 33%.
- INNOGLOBAL Programme: CDTI aid will be in the form of a grant.

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Figures

Figure 1: Cluster Logo

What can CDTI do for R &D& I activities in Spanish nanotechnology companies?

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The Centre for Industrial Technological Development (CDTI) is a Public Business Entity, answering to the Ministry of Economy, Industry and Competitiveness, which fosters the technological development and innovation of Spanish companies. It is the entity that channels the funding and support applications for national and international R&D&i projects of Spanish companies. The CDTI thus seeks to contribute to improving the technological level of the Spanish companies by means of implementing the following activities:

- Financial and economic-technical assessment of R&DI projects implemented by companies.
- Managing and fostering Spanish participation in international technological cooperation programs.
- Fostering international business technology transfer and support services for technological innovation.
- Supporting the setting up and consolidating technological companies.

The CDTI employs over 300 people, three quarters of whom are engineers and graduates. Even though the bulk of the CDTI infrastructure is in Madrid, the Centre offers Spanish companies a strategic network of offices or representatives abroad to support their international technology activities.

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[1] http://www.cdti.es

Figures

Figure 1: CDTI Logo

Figure 2: CDTI Activity

Selection of proven risk management measures (RMMs) to control the exposure to ENMs

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Current knowledge on the effectiveness of personal protective equipment (PPE) and technical measures against nanomaterials is still scarce. However, a number of initiatives, including EU funded research projects and studies from research organizations across the scientific community are starting to appear.

This work presents experimental data on the effectiveness of respiratory protective equipment, chemical protective gloves, protective clothes, and local exhaustive ventilation (LEV) systems to control the exposure to ENMs in occupational settings.

New experimental data on the protection factors achieved under representative exposure scenarios, as well as recommendations for the design of PPE and engineering controls will be presented.

The experimental studies were conducted by means of standard operation procedures (SOPs) developed on the basis of current EN standards , and recommended approaches retrieved from peer reviewed publications.

Concerning PPE, the data retrieved showed that Full and Half Mask Respirators provided adequate performance levels of filtration efficiency against NMs (figure 1). Total inward leakage (TIL) ratios determined in relevant studies suggest that face seal leakage, and not filter penetration, is a key parameter to be considered when working with ENMs.

In the case of protective gloves, performance depends strongly on the material of the glove, and although generally there are no pores in their surface, some small defects or gaps can be enough to offer a way in to the glove.

Finally, the performance of LEV systems showed a decrease in efficiency when the distance from the source increases from 0 to 65 cm. With a vertically positioned hood efficiency decreases gradually at 5 cm and drops significantly at 20 cm. At 45 cm a more or less similar efficiency is measured compared with 5 cm efficiency (figure 2).

Figures

RPD	Specifications	Measures	Standard Efficiency	Protection (NMs)	Reference particle
Filters	P2 Filter	Efficiency	94 %	99.83 %	NaCl
	P3 Filter	Efficiency	99.95 %	99.97 %	NaCl
Half Mask	New Mask P3 Filter	Efficiency	99.95%	99.47 ± 0.83 %	NaCl
	Aged Mask P3 Filter	Efficiency	99.95%	99.77 ± 0.29 %	NaCl
Full Mask	New Mask P3 Filter	Efficiency	99.95%	99.73 ± 0.25 %	NaCl
	Aged Mask P3 Filter	Efficiency	99.95%	99.78 ± 0.16 %	NaCl
FFP	FFP1	Efficiency	80%	75.63 %	NaCl
	FFP3 (Model a)	Efficiency	99%	99.77 ± 0.29	NaCl
	FFP3 (Model b)	Efficiency	99%	95.63 ± 4.39	NaCl

Figure 1: Effectiveness of common RPE when dealing with ENMs.

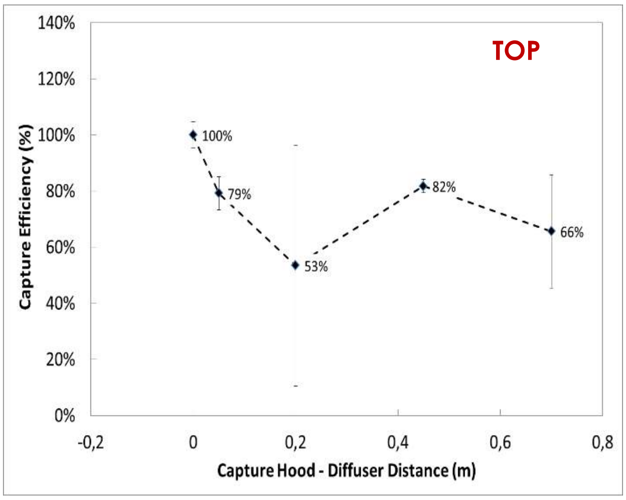

Figure 2: Capture efficiency of LEV systems

Graphene electrodes for capacitive deionization: an energy efficient water desalination method

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With 1.8 billion people predicted to live in areas of extreme water scarcity by 2025, desalination—the removal of salt from water—is increasingly being proposed as a solution. Now reverse osmosis (RO) and multistage flash distillation (MSF)are the most common used desalination techniques, but their cost and energy consumption are limiting factors of these technologies. The capacitive deionization (CDI) is an emerging method with reduced use of energy and therefore with lower costs [1].

The development at TECNALIA of novel CDI electrodes based in three-dimensional rGO with incorporated metal oxide nanoparticles (rGO/MOx) has led to excellent results of high specific capacitance and good electrosorption capacity. This hybrid RGO/MOx is a promising material to improve the actual CDI technology in order to compete with RO technology for water desalination. Laboratory tests have demonstrated good performance and theoretical estimations of energy consumption are far below the values achieved by the RO technology.

This work has been developed in the framework of the EU Graphene Flagship Project (GA 696656).

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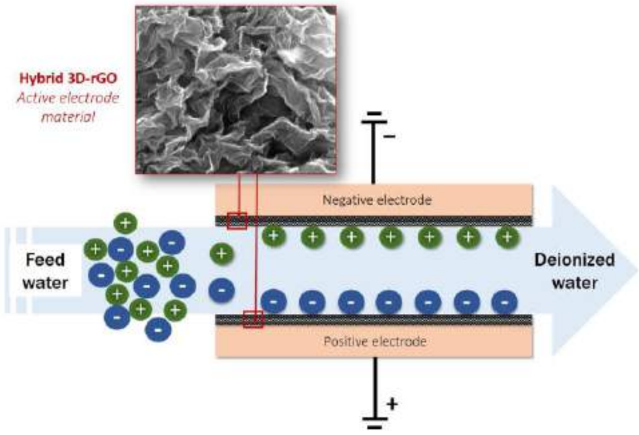

Figure 1: CDI desalination technique including 3G-rGO electrodes

SIESTA-PRO: Professional Software Ready for Industry

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Abstract

Simune Atomistics S.L. (SIMUNE) [1] is a company launched in 2014 as a joint venture of a group of scientific experts and the Nanoscience Cooperative Research Center CIC nanoGUNE (www.nanogune.eu). SIMUNE was created to capitalize the experience and know-how of a group of scientists, international experts in computational simulations of materials(http://www.simune.eu/index.php/about-us).

In 2015, SIMUNE established a strategic partnership with SIESTA[2]. SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) is both a method and its computer program implementation, to perform efficient electronic structure calculations and *ab-initio* molecular dynamics simulations of molecules and solids.

This workshop will cover the SIESTA package, the product SIESTA-PRO, and the support service offered by SIMUNE. SIESTA-PRO is the Commercial Software currently under development by SIMUNE on top of the existing SIESTA code to facilitate the professional use of the SIESTA code.

The main capabilities implemented on the current version of the SIESTA code, as well as the features under development will be presented.

Next, the SIMUNE protocols for the generation of pseudopotentials and the construction of basis sets of strictly localized numerical atomic orbitals will be introduced.

Finally, a detailed view of the post-processing SIESTA-PRO analysis tool will be given.

References

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Acknowledgments

SIMUNE has received funds to develop the project: SIESTA -PRO - Spanish Initiative for Electronic Simulations with Thousands of Atoms: Open Source code with professional support and warranty. The project (RTC-2016-5681-7) has been funded by the Spanish Ministry of Economy, Industry and Competitiveness and has been co-financed by the European Structural and Investment Funds with the objective to promote the technological development, innovation and quality research.

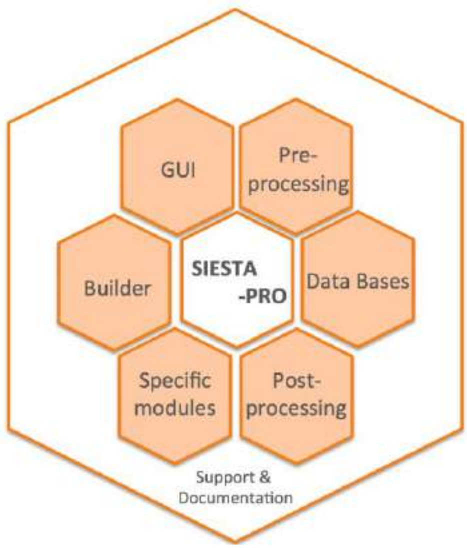

Figure 1: Schematic representation of the modules constituting SIESTA-PRO

Opportunities for Nanotechnology and Nanomaterials in Horizon2020

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Horizon2020 is the biggest EU Research and Innovation programme ever with nearly €80 billion of funding available over seven years (2014-2020).
In this programme, Nanotechnology is recognised as one of the Key Enabling Technologies (KETs), with applications in multiple industries and which can help to tackle the societal challenges. However, the market uptake of nanotechnology and nanomaterials has still some technology and regulatory barriers to overcome.

Horizon2020 is arriving at its final phase, with its last work programme 2018-2020 launched in October last year. Opportunities for Nanotechnology can be found mainly in the thematic area NMBP(Nanotechnologies, Advanced Materials, Biotechnology and Advanced Manufacturing and Processing), which in this last WP has a call titled "Foundations for tomorrow´s industry", with a total budget of €395 M. This call is devoted to facilitate the arrival to the market of innovations, creating an effective innovation ecosystem, as long as growth and jobs. A new concept, the *Open Innovation Test Beds*, will establish a network of infrastructure and services for the design, development, testing, and upscaling of nanotechnology and advanced materials. Characterisation, computational modelling, risk assessment and regulatory aspects can also be found in this call.

Horizon2020 gives excellent opportunities for collaborative research, and, beyond funding, for internationalization and gaining recognition and an outstanding position at a European level.

References

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Figures

Figure 1: Horizon2020 is the European Program for research and innovation (2014-2020).

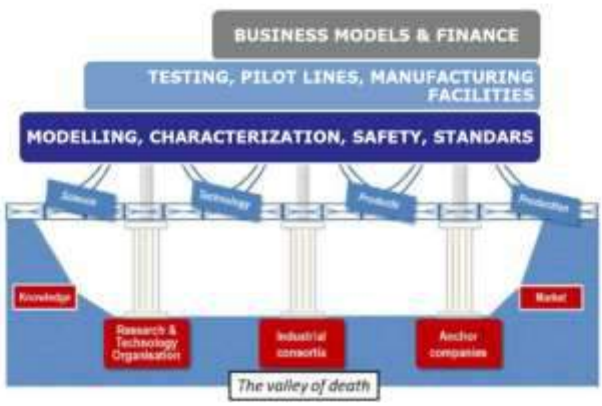

Figure 2: Bridging the valley of death by means of addressing specific aspects for nanomaterials engineering and upscaling.

FIB processing using Elphy: some examples

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Abstract

The Barcelona Microelectronics Institute (IMB) is the Barcelona location of the National Microelectronics Center (CNM). It belongs to the Spanish Research Council (CSIC).

IMB-CNM holds the largest Integrated Clean Room for Micro and Nano fabrication in Spain. It is a Large Scale Facility (ICTS) dedicated to the development and application of innovative technologies in the field of Microelectronics together with other emerging Micro/Nanotechnologies, and it is equipped with state of the art equipment for micro and nanofabrication.

In this work we are presenting some of the activities performed with our focus ion beam (FIB) system. It is a 1560XB CrossBeam system from Zeiss equipped with Ga^+ ions, gas injection system (GIS) for enhanced etch and local deposition, three nanomanipulators for electrical probing and TEM lamellae preparation and an ELPHY Quantum attached system for lithography purposes.

With the ELPHY Quantum system is possible to control the ion beam for nanofabrication of devices by ion implantation and/or milling by fine tuning the dose and precise control of beam positioning [1][2].

References

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Figures

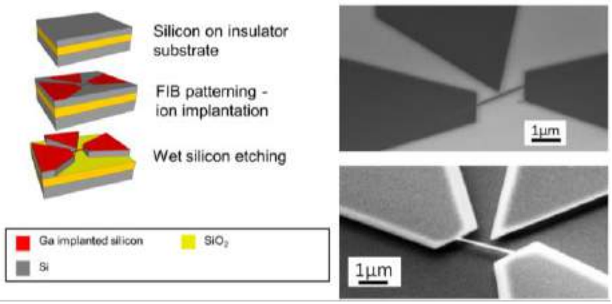

Figure 1: *Left*: definition of structures by means of Ga^+ ion implantation and subsequent wet etching of the silicon to form the final structure.
Right: SEM images previous to the wet etching and after the wet etching.
As can be seen in the first image the substrate is exposed with Ga^+ ions using ELPHY Quantum software, obtaining a patterned substrate with our desired design. In the second image, it can be observed the released structures after the wet etching. Big exposed areas are still attached to the bulk substrate (darker areas) but the smaller resonator is just hanged by the bigger areas. The fine dose tuning and the correct energy selection allows to create these structures very precisely.

Industry 4.0 concept for Nano-Enabled Products manufacturing pilot plants for Automotive and Aeronautics

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This presentation shows a vision of how Industry 4.0 concepts can help Pilot Plants in the Nano-Enabled Products manufacturing, to speed-up the improvement from TRL 6-7 to TRL 9 in Automotive and Aeronautic sectors.

Built-in quality, process stability (by means of process knowledge and domain), TRL increase speed-up and Environment, Health and Safety aspects are the drivers of Industry 4.0 implementation in NEP Pilot Plants.

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Figures

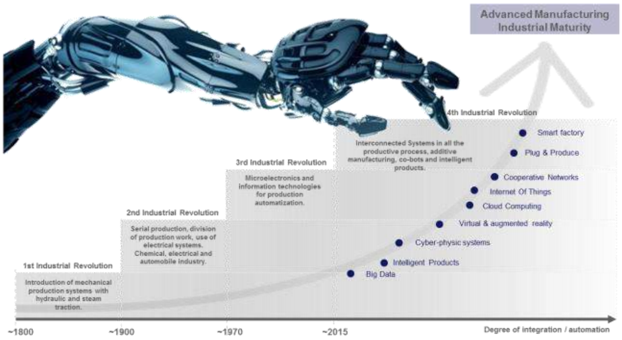

Figure 1: Set of tools and technologies available in Industry 4.0

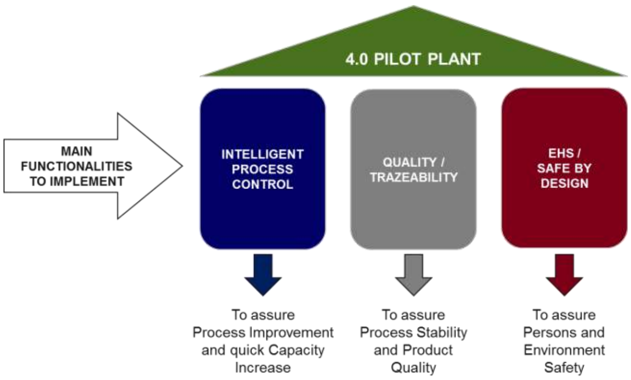

Figure 2: Main functionalities to improve in NEP Pilot Plants

Excited states properties for SIESTA calculations: time-dependent density functional theory and beyond.

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Electronic excited states in condensed matter govern many physical phenomena important for industrial applications. Such phenomena as light-matter interaction and particle-matter interaction are cricial for the operation of light-emitting diodes and photo-voltaic cells as well as for undestanding the outcomes of many spectroscopical techniques existing today. In this talk, we present the algorithms and programing solutions for SIESTA users allowing to estimate the light-absorption spectra and electron energy loss spectra within time-dependent density functional theory (TDDFT). TDDFT is a rigorous extension of density-functional theory (DFT) which is implemented in SIESTA using the parsimonious basis of numerical atomic orbitals (NAO). The algorithm relies on an iterative computation of the electron density induced by an external perturbation [1]. We use the formalism of linear response functions which is more computationally efficient than the propagation of wave-packets – the alternative method to realize TDDFT calculations developed in SIESTA. The efficiency of the linear response TDDFT allows to estimate the light absorption and electron energy loss spectra [2] of large molecules, quantum dots and metallic clusters [3,4,5] containing thousands of atoms. SIESTA is a DFT package with built-in molecular dynamics (MD) capabilities. Coupling the ab-initio MD with TDDFT allows to estimate the effects of thermal motion on the electronic spectra. The speed of our TDDFT implementation makes feasible to perform a configuration average of the optical absorption spectra [1].
Our code is written mostly in Python language allowing for a quick and compact implementation of most numerical methods and data-managing tasks with the help of Numpy/Scipy libraries and Python intrinsics. Part of the code is written in C and Fortran to achieve a competitive speed in particular sections of the algorithm. Many parts of the current algorithm and implementation are useful in other ab-initio methods for electronic excited state properties, such as Hedin's *GW*, Bethe-Salpeter equation and DFT with hybrid functionals. Corresponding proof-of-principles implementations are already part of the code and will be shortly covered in the presentaion.

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HYPROD: The Smart composites platform towards advanced functionalization of smart lightweight components for automotive and aeronautics

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To answer the need for new solutions combining high performance and high throughput processes, IPC has developed with its partners newhybrid solutions (thermoplastic composite overmoulding) to produce net-shape lightweight semi-structural parts with an advanced functionalization.
Going one step further, the "smart composites" Pilot Lines were set-up to increase functionality of composites parts by integrating new features to FRPs.
This development answers the need for continuous monitoring of structural composite parts to guarantee user safety. It opens the way to improved competitiveness of composite solutions against other materials by increasing function integration with an underlying mass-production approach.
With this breakthrough Pilot Lines, IPC is developing a wide array of integrated smart solutions - covering various technological approaches and functions: sensing, identification, anti-icing, etc - for automotive and aeronautics applications.

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Figures

Figure 1: Composite cowl panel produced in the frame of the ARIZONA project (French National project, 2013-2017)

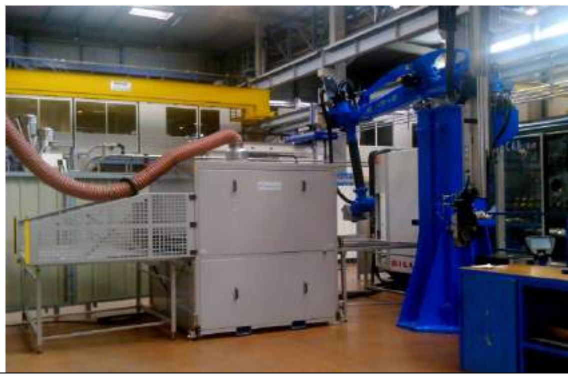

Figure 2: Pieces of equipment of the HYPROD platform

Functionalized Processable Graphene from Electrochemical Approaches

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The rapid rise of 2D materials over the past decade evidences not only a basic scientific interest but also their potential technological impact, as they might play a ground-breaking role in future electronics, printed circuits and sensors, wearable applications, composites and the storage and utilization of clean electric power obtained from renewable resources.
For graphene however, there has been a gap between laboratory-scale research and commercial applications for a long time due to the lack of reproducible bulk production methods at low cost level. Today many of these challenges seem solved, with production capacities reaching ton scale for both graphene and graphene oxide materials and the first products established on the market. However, there are still challenges, especially when it comes to processing. Liquid phase exfoliation techniques for instance, can provide high quality products with low defects, but the sheets are small and need surfactants or other additives to avoid restacking, which are difficult to remove and can reduce matrix-interactions and final conductivity. In contrast, graphene oxide lacks electrical conductivity and the outstanding mechanical properties of graphene, but can be dried and redispersed and therefor shows significant advantages in terms of processability. Due to its high density of functional groups GO can also be easily functionalized for different purposes.
The electrochemical preparation of graphene combines the best of both worlds. With our recent advances in the simultaneous electrochemical production and functionalization, we are able to provide a new generation of processable, yet high quality few-layer graphenes. Depending on the process conditions, a tuneable level of defects and defined functional groups can be introduced, that improve processability while maintaining a good electrical conductivity and reasonable sheet size.

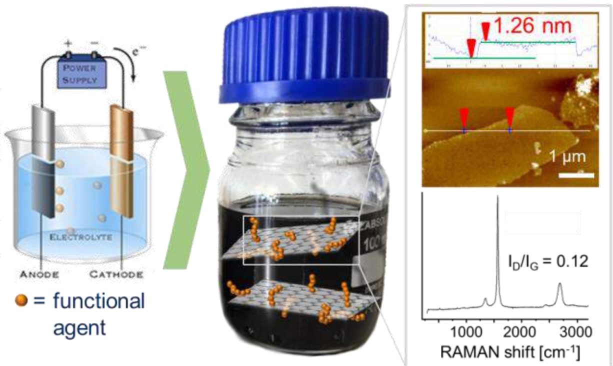

Figure 1: Surfactant-free aqueous dispersion of high quality functionalized few-layer graphene.

Combined with a scalable and eco-friendly process technology we are opening up new possibilities and prospects for the applications graphene, mainly in the field of inks, composites, electronics, energy storage and energy conversion.

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PLATFORM: Safe-by-design framework for the development of new pilot lines for the manufacture of carbon nanotube-based nano-enabled products for automotive and aeronautics

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Abstract

To make the leap between the pilot production and the commercialization of nano-enabled products (NEPs) in the European market (TRL9), the compliance with the safety regulatory requirements represents a major challenge, not only in terms of product safety, but also with respect to the manufacturing lines (safe production).

The Machinery Directive 2006/42/EC (MD) – transposed to the respective national legislations – is the EU regulatory framework applying the safe-by-design of new machinery. The Directive establishes the mandatory Essential Health and Safety Requirements (EHSRs) to be fulfilled by each machine, while detailed technical specifications for compliance are given in harmonized standards (HSs).

However, there are no specific EHSRs for nanosafety, nor HSs to guide the safe design of machinery for the manufacture of NEPs, or for the prevention and control of nanosafety risks involved in the design of such machinery.

In this context, this paper presents the experience gained by the European project PLATFORM (GA 646307) in the safe-by-design of three new manufacturing pilot lines (PPLs) for the industrial production of carbon nanotube-based nano-enabled products (bucky- papers, CNT-doped prepregs and CNT-doped veils); as intermediate NEPs for the manufacture of structural components with improved properties, for aerospace, automotive, military, medical and electronics industries.

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Strategies on technology transfer and patents commercialization for nanotechnology at the Spanish National Research Council

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The Spanish National Research Council (CSIC), an outstanding generator of scientific knowledge in Europe, has designed and implemented a series of actions in order to take advantage of the knowledge generated in nanotechnology by its research groups by mean of an appropriate transfer to both the Spanish and the international industry. CSIC's strategy has been particularly successful, both in the number of filed patents and in the number of licensed patents and created spin-off companies in the nanotechnology field. Our analysis shows that very successful results can be achieved in technology transfer when the appropriate resources are available and properly organized with an adequate combination of efforts in knowledge protection, promotion and commercialization of technologies and support to the scientific entrepreneurs of the institution.

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Figures

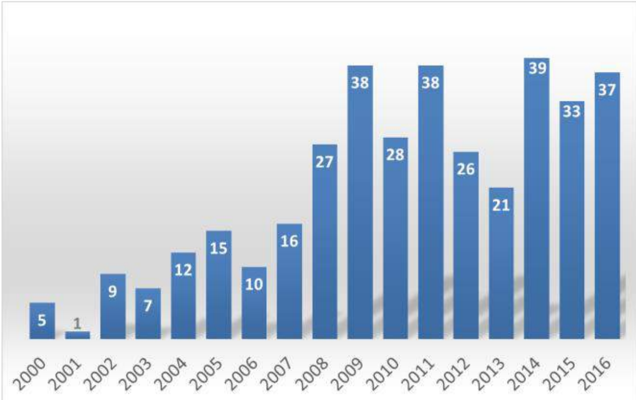

Figure 1: Number of CSIC's technologies protected by patent application or trade secrets in nanotechnology from 2000 to 2015

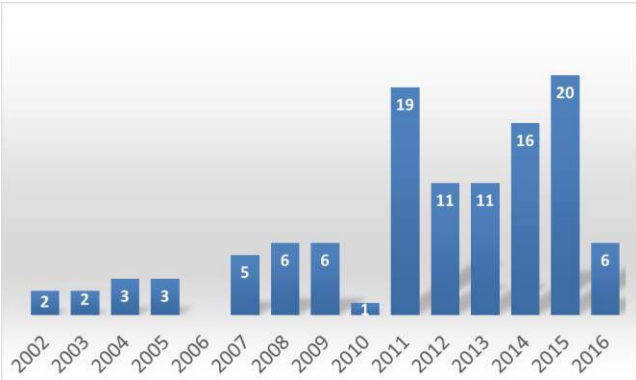

Figure 2: Evolution of the number of nanotechnologies protected by patent or trade secret licensed by CSIC over the period 2002-2015.

SIESTA-PRO: Professional Software Ready for Industry

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Abstract

Simune Atomistics S.L. (SIMUNE) [1] is a company launched in 2014 as a joint venture of a group of scientific experts and the Nanoscience Cooperative Research Center CIC nanoGUNE (www.nanogune.eu). SIMUNE was created to capitalize the experience and know-how of a group of scientists, international experts in computational simulations of materials(http://www.simune.eu/index.php/about-us).

In 2015, SIMUNE established a strategic partnership with SIESTA[2]. SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) is both a method and its computer program implementation, to perform efficient electronic structure calculations and *ab-initio* molecular dynamics simulations of molecules and solids.

This workshop will cover the SIESTA package, the product SIESTA-PRO, and the support service offered by SIMUNE. SIESTA-PRO is the Commercial Software currently under development by SIMUNE on top of the existing SIESTA code to facilitate the professional use of the SIESTA code.

The main capabilities implemented on the current version of the SIESTA code, as well as the features under development will be presented.

Next, the SIMUNE protocols for the generation of pseudopotentials and the construction of basis sets of strictly localized numerical atomic orbitals will be introduced.

Finally, a detailed view of the post-processing SIESTA-PRO analysis tool will be given.

References

[1] www.simune.eu
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Acknowledgments

SIMUNE has received funds to develop the project: SIESTA -PRO - Spanish Initiative for Electronic Simulations with Thousands of Atoms: Open Source code with professional support and warranty. The project (RTC-2016-5681-7) has been funded by the Spanish Ministry of Economy, Industry and Competitiveness and has been co-financed by the European Structural and Investment Funds with the objective to promote the technological development, innovation and quality research.

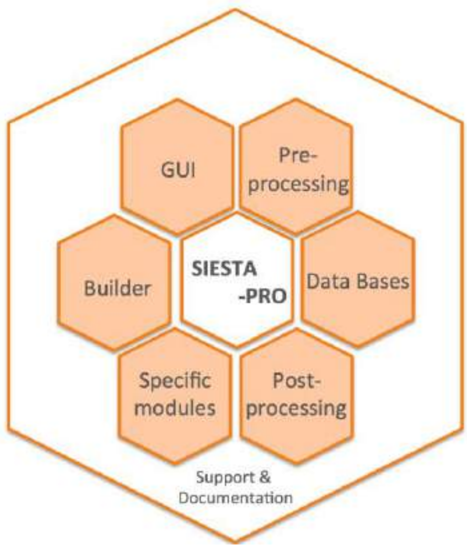

Figure 1: Schematic representation of the modules constituting SIESTA-PRO

Nanoreg2 SbD case study: Carbon nanofibres produced by the floating catalyst technique

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Safe by Design Grupo Antolin case study in Nanoreg2 project is based on the production of carbon nanofibres by the floating catalyst method focusing on two products GANF and GAtam and with the aim of choosing the most suitable option for the scale-up considering SbD aspects. The main differences between the two nanomaterials are the specific surface area, surface functionalization characteristics, and degree of graphitization or crystallinity.

The case study has been developed and arranged in the following tasks:

1) Risk assessment (RA) before the SbD: Selection and application of preliminary risk assessment tools at all points of the production process of both GANF and GAtam. Gaps in information and hot spots for SbD were identified in this way.

2) Design and implementation of a safer process: Different possibilities were studied in the hot spots identified in task 1 for making the production process safer. The best possibility is currently being simulated / implemented in the industry. The gaps in information identified in task 1 are being filled.

3) RA after the SbD: With the tools selected from the SIA toolbox a risk assessment is being performed after the implementation of the design to make it safer.

4) Life Cycle Analysis (LCA): The LCA is being done before and after the SbD in order to determine the improvements during all the life of the product.

5) Socioeconomic analysis (SEA). The results of both RA and LCA will feed a socioeconomic analysis where the improvements made will be measured in terms of benefits.

There are also limitations from the point of view of grouping carbon nanofilaments. Carbon nanotubes are very resilient structures extremely difficult to be shortened due to their co-cylindrical distribution of basal or graphene planes along their fibre axis. On the other hand, CNTs present a highly hydrophobic and chemically inactive surface hard to be functionalized due to the absence of basal plane edges or defects.

Any kind of carbon nanofilament with different structural arrangement of basal planes than co-cylindrical are considered CNFs. They present numerous basal plane edges and defects on their surface that favour their surface functionalization and wettability. Besides, CNFs are very sensible to physical forces applied against van der Waals bonding between basal planes leading to exfoliation phenomena and fibre shortening.

It is also necessary to consider that carbon nanofilaments grown by c-CVD techniques present a certain content of catalyst nanoparticles content as metal impurities. These metal nanoparticles play also an important role from the point of view of SbD barriers.

Why FIB for Nanofabrication ?
Advanced Applications and New Ion Species

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An increasing number of applications use focused ion beam (FIB) systems for nanofabrication and rapid prototyping tasks. FIB nanofabrication is a good partner to other lithography techniques providing complementary strengths like direct, resistless, and three-dimensional patterning.

Although a FIB process can in many cases be slower than a resist-accelerated process, the relative simplification of the nanofabrication approach, especially for the direct processing of novel materials, helps to achieve scientific results faster. We report on our continuous effort to advance FIB technology along with an instrumentation platform dedicated to nanofabrication requirements.

The nanofabrication requirements for FIB technology are specific and more demanding in terms of stability, resolution. We have improved gallium-based liquid metal ion source (LMIS) with a stable gun emission design enabling long-term stability, and producing low drifts in probe current and beam position.

Combining this FIB technology with an instrumentation platform optimized for nanometer scale patterning over large areas and extended periods of time applications such as X-ray zone plates, large area gratings, plasmonic arrays, and wafer-scale nanopore devices become possible.

Moreover the type of ion defines the nature of the interaction mechanism with the sample and has significant consequences on the resulting nanostructures. Therefore, we have extended the technology towards the stable delivery of multiple ion species selectable into a nanometer-scale focused ion beam by employing a liquid metal alloy ion source (LMAIS). This provides single and multiple charged species of different mass, e.g. Si, Ge or Au, resulting in significantly different interaction mechanisms. We present and discuss the capabilities of the instrument for sub-20 nm nanofabrication as well as potential applications.

Figures

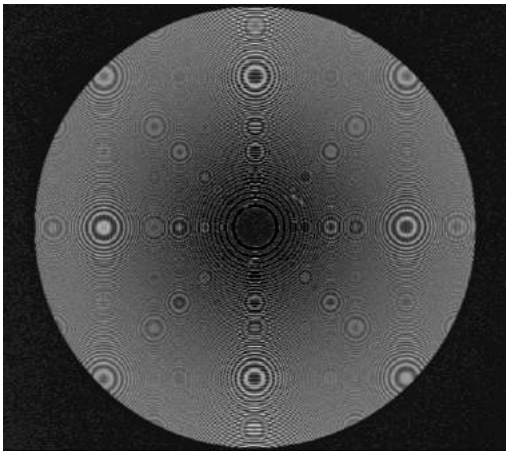

Figure 1: 100µm Dia zone plate on membrane

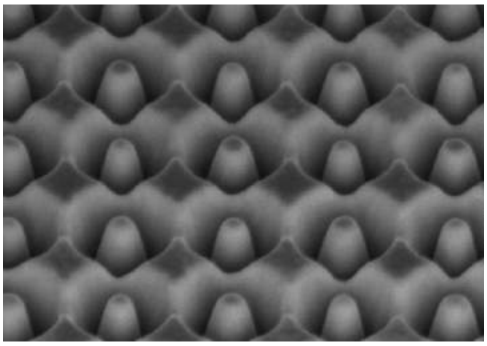

Figure 2: True Direct 3D FIB Patterning

Grouping of nanomaterials as a previous step for safe by design, registration and risk assessment: an approach based on ecotoxicity data in H2020 project NanoReg2

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Manufactured nanomaterials (MNs) with the same core chemical composition can show an enormous variety of forms depending on their shape, size, specific surface, crystallinity, and other physicochemical properties. In addition, the presence of coatings constitutes an additional source of variability that complicates even more the general vision of the field. Since MNs must be registered for their commercialization and its possible risk for the human health and the environment must be assessed, it is essential to look out for strategies that could simplify these regulatory processes considering the continuously growing number of MNs. In addition, this grouping exercise can be very useful in safe-by-design approaches establishing those collections of MNs that can be more susceptible of improvements. Taking all this into account, in the framework of the H2020 NanoReg2 project we have generated ecotoxicity data of a set of nanomaterials in order to perform a grouping exercise that also considers basic physicochemical properties. Ecotoxicity data for a set of MNs have been produced in vitro and in vivo using fish and mussel cells, Daphnia, algae and mussels. Some hypothesis for grouping were generated and statistical approaches are being applied in order to establish appropriate MNs groups.

Device Optimization by Smart Nanopatterning Strategies Using Focussed Electrons and Ions

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Multi-technique electron beam lithography (EBL) systems or other nanofabrication instrumentation comprising both an electron and an ion beam optics (SEM/FIB tools) have proven to be flexible multi-purpose tools covering a broad range of nanotechnology applications. They are regarded as a "must have" in today's research and development based laboratories of various disciplines. These techniques routinely provide nanopatterning resolution with sub 10nm feature sizes and are well suited for nano-research - excellent beam control provided. In order to secure stable, reproducible, highest precise and efficient operation for optimum results and device performance, advanced patterning control and strategies for these tools come into play. Only by exploiting innovative, dedicated nanofabrication hardware and software architecture, their true nanopatterning potential can be fully unlocked.
In this talk, we will focus on the optimization of three application classes/categories, which are typical and representative for a large group of nanofabrication tasks:
(1) Eliminating stitching errors in extended patterns exceeding typical write field sizes by far.
As an example, we present high performance waveguides and large area gratings that are fabricated using unique "continuous writing modes"
(2) Securing maximum pattern placement accuracy and optimum shape definition during long term ion beam induced nanofabrication processes.
For nanofabrication of a "perfect" photonic crystal, excellent drift compensation control, material redeposition avoidance and application specific directional nanopatterning modes have been applied.
(3) Nanofabrication of 3D-deposits and freely suspended nano-devices.
Exploiting "patterning on image" algorithms and specific directional scanning/nanopatterning modes ("FLEXposure") can be very helpful for straightforward and successful fabrication of true nano-electro-mechanical devices.

Figures

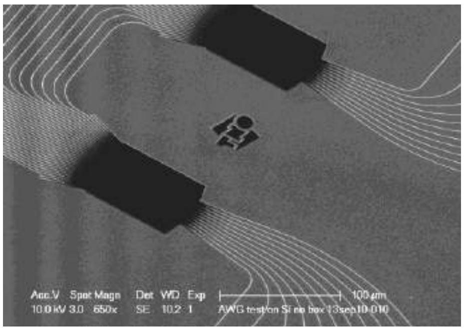

Figure 1: Arrayed Waveguide Grating (AWG) with couplers using "continuous writing modes"

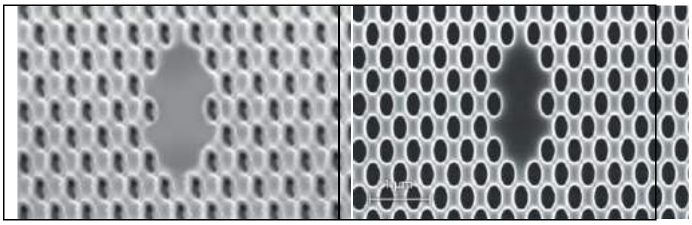

Figure 2: Photonic crystal milled without and with optimized patterning strategy

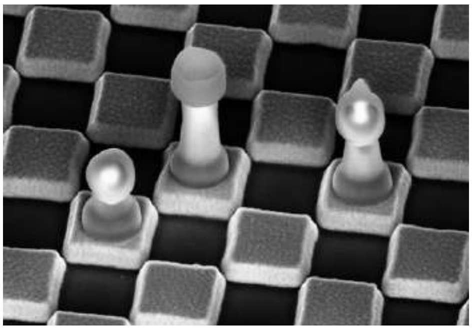

Figure 3: 3D deposit using specific directional scanning/nanopatterning modes

Improving Li battery performance with graphene and GO

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Abstract

Graphene Batteries AS is working towards the commercialization of two technologies for energy storage devices, a proprietary graphene coated Al foil for energy storage devices and sulphur cathode for LiS batteries which have shown promising results in laboratory scale coin cell.

Cathodes of Li-ion batteries are made on Al foils as current collector. The interphase between the foil and the electrode past defines the electrode impedance especially at high current drains [1]. Our coated foils tested with $LiFePO_4$ cathodes demonstrated >80% capacity retention at 10C discharge rate outperforming uncoated foils and commercial cathodes (Fig. 1).

Li-S batteries are considered among the most promising candidates to achieve high energy density at low cost [2]. Our sulphur cathode tested against Li foil delivered increasing areal capacity of ~2 mAh/cm^2 over cycling with 4 $mg.S/cm^2$ active material loading. Current effort is directed towards increasing the sulphur utilization to yield 5 mAh/cm^2 for >200 cycles. Next, these results will be demonstrated on larger format cells where we can explore scalability issues and reliably extrapolate performance metrics of the final cells.

References

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Figures

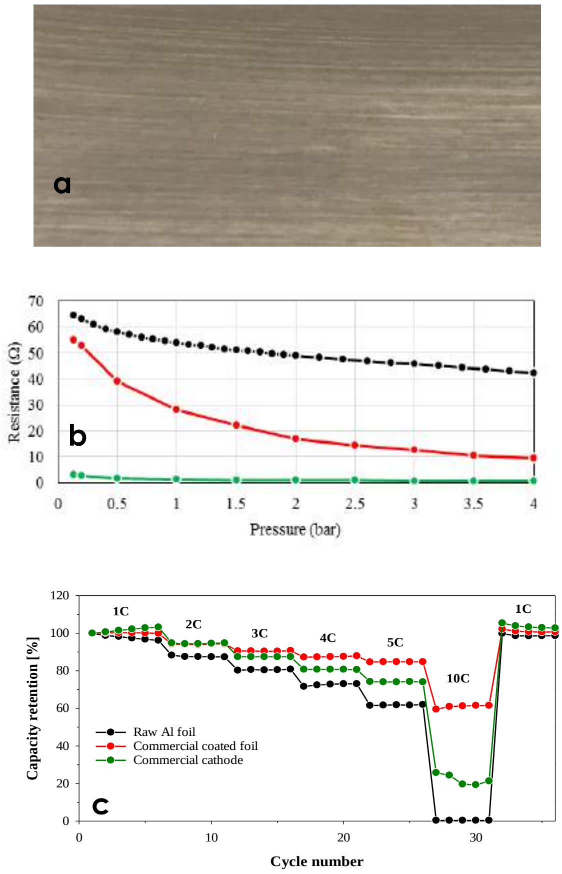

Figure 1: a) Graphene coated Al foil, **b)** Sheet resistance under pressure, **c)** comparative cycling results.

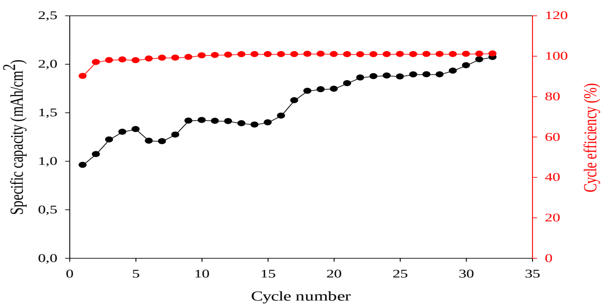

Figure 2: Cycling performance of LiS cell at 0.2C rate.

ESTCRATCH Pilot- Example of Application for the Automotive Sector with improved Scratch Resistance and Non-Conventional Aesthetics based on Nanotechnologies

Mario Ordóñez. New Materials Responsible MTC R+D+i Department
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ESTCRATCH Pilot from Izadi-Nano2Industry project is an industrial prototype demonstrator of an automotive application made by injection of PMMA with improved scratch resistance and non-conventional diffractive/plasmonic aesthetics based on nanotechnologies.

A new formulation of PMMA nanocompound, patent pending, has been developed to improve the scratch and mar resistance by adding nano-additives at the extrusion step. Pre-industrial trials have been run to produce nanobatches and PMMA nanocompund.

Sample parts made of PMMA nanocompound has been injected at industrial scale to evaluate their processability and general performances, including aesthetics, chemical, mechanical and thermal properties.

A prototype version of a B-Pillar has been developed as demonstrator of automotive application with non-conventional aesthetics. The design is based on an exterior trim, with high gloss, deep black finish. Technical requirements are according to the standard quality levels of the European market. Diffractive/plasmonic aesthetics of the ESTCRATCH B-Pillar based on the nanotexturing of the injection moulds. Injection trials at industrial scale have been done to optimize processing conditions, quality of the replicas, and durability of the nanotextured surfaces of the mould. Preliminary evaluation tests have been done to verify the performance of the parts, according to the functional specifications from European car makers.

Acknowledgement
Financial support by the EU Commission through Project H2020-686165-IZADI-NANO2INDUSTRY is gratefully acknowledged.

References

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[2] Danmarks Tekniske Universitet
[3] NILT Technology APS
[4] Sematec
[5] Sisteplant
[6] Cemecon Scandinavia AS
[7] Michael Lundbech

Figures

Figure 1: Nanotextured diffractive IZADI logo on top side of the ESTCRATCH B-Pillar.

Guidance for SbD implementation in the Nanotechnology Industry

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The development of a SbD strategy requires both reliable models that correlate physicochemical properties of nanomaterials to their safety and functionality but also robust decision criteria to effectively guide the SbD process. As a synthesis of the acknowledgment gained in the Nanoreg II project a guidance has been developed to aid the application of the SbD concepts through the industrial nanotechnology community, with a special emphasis to making the application of SbD affordable to SMEs.

Safe by design, Risk assessment and Risk governance in industry

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The idea behind safe by design (SbD) is to integrate knowledge of nanomaterials' potential adverse effects into the process of designing nanomaterials and nanoproducts—and to engineer these undesirable effects out of the respective materials or products. This entails that functionality and safety be considered in an integrated way right from the earliest phases of the research and innovation process. Several European Initiatives are dealing with this concept, its implementation in industry and ultimately its inclusion in a new versatile risk governance framework. In the NanoReg2 project, Risk Assessment tools and Life Cycle Assessment are being used to identify "hot spots" for SbD in the industry and gaps in knowledge as well as to demonstrate the effect of the SbD implementation. In the caLIBRAte project the aim is to establish a versatile risk governance framework for assessment and management of human and environmental risks of MN and MN-enabled products. This framework will include nanospecific models (control banding qualitative and other quantitative models) that will be calibrated and refined so that they will be useful for SbD and Risk Management Decision Support.

The Safe-by-Design concept and its application in industrial innovation processes

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The Safe by Design concept for nanomaterials has been developed by TEMAS and others under different flagship European initiatives to cover uncertainties and risks regarding nanomaterials [1]. To materialise this concept, the Safe by Design Implementation Platform was subsequently developed by TEMAS as a web-based management structure, to support industry working with nanomaterials both in processes and product development (Fig 1). The final aim being that safer products arrive to the market in a cost-efficient manner, always taking into account hazard and exposure issues to workers, consumers and environment. The Platform is Regulatory driven and fed by both hard regulation (REACH, Occupational Health, Cosmetics, Biocides, Pesticides) and soft regulations [Life Cycle Assessment (LCA) and Socio-Economic Analysis (SEA)] anticipating future requirements, so users are better prepared for upcoming regulations in a cost-efficient way (Fig 2-3). The Platform can be used at different innovation processes and with different applications. Examples of how to use the Platform in different developmental settings and regulatory contexts will be provided within the "Safe by Design Implementation: Industrial experiences from European Initiatives" workshop and will cover 1) Safety on industrially driven processes, 2) Selection of materials for product development and 3) Regulatory driven use for final products.

References

[1] Gottardo S. et al. JCR Science for Policy Report April 2017

Figures

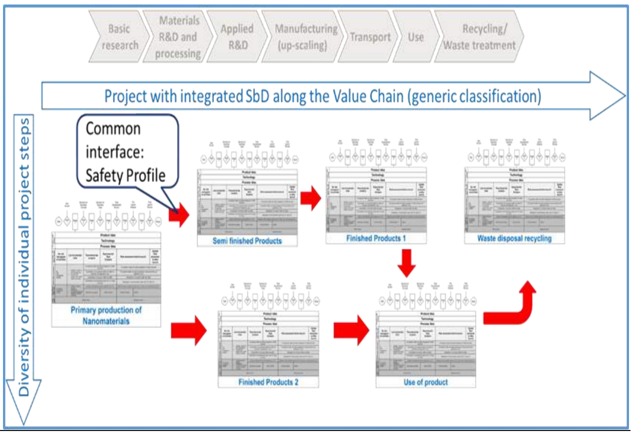

Figure 1: Workflow of the Implementation Platform along the value chain of a product

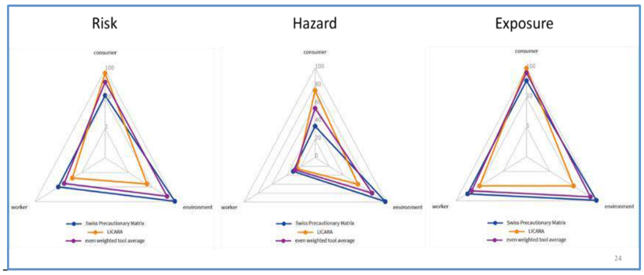

Figure 2: Outcomes from different Risk Assessment tools compared by the Platform

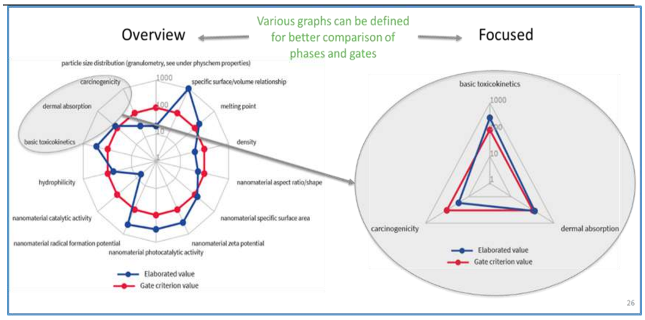

Figure 3: The Platform is fed, with both regulatory accepted toxicological values (gate keepers, red) and experimental values (from case study, blue). The customer can assess at any time the position of their product/process compared to the accepted/regulatory situation

Technology and processes for scaled up fabrication of 2D materials and heterostructures

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Abstract

Vapour deposition techniques have gained a lot of interest for growth of two dimensional (2D) materials[1-4]. In the recent past there has been a surge in the number of researchers studying atomic planes of other Van der Waals solids and heterostructures created by stacking layers with complementary characteristics to achieve novel functionality [5]. For successful scaling up of prototypical applications demonstrated to date, technologies and processes for large area deposition of these materials need to be developed. In this talk I will first give an overview of technologies and processes developed at Oxford Instruments towards growth of 2D materials and heterostructures by CVD and ALD followed by our developments in technology for device fabrication processes such as dielectric deposition and device pattern etching.

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