NanoSpain Conf 2019

May 28-31, 2019 • Barcelona (Spain)

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IN SPAIN

ABSTRACTS BOOK

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NanoSpain Conf 2019

May 28 -31, 2019 • Barcelona (Spain)

Consolidated as a reference meeting of Nanoscience and Nanotechnology (N&N) in Spain, the NanoSpain2019 conference is not limited to a conventional presentation of ideas or results, but seeks to deepen the common themes among the participants, also serving as a link between industry and researchers.

Since 2004, year the event was launched, NanoSpain conference series is now an established and well-known meeting in Spain, aiming to agglutinate and coordinate the efforts made in the field of the Nanotechnology by Spanish groups from universities, research institutes and companies.

NanoSpain events facilitate the dissemination of knowledge and promote interdisciplinary discussions not only in Spain but among the different groups from Southern Europe.

Over the past years, NanoSpain conference became more and more multidisciplinary and 2019 won't be an exception. NanoSpain2019 will cover a broad range of current research in Nanoscience and Nanotechnology.

NanoSpain2019 will offer a multitude of renowned international Keynote and Invited speakers, contributed talks, posters and a commercial exhibition.

We would like to thank all participants, speakers, sponsors and exhibitors that joined us this year.

Finally, thanks must be directed to the staff of all organizing Institutions.

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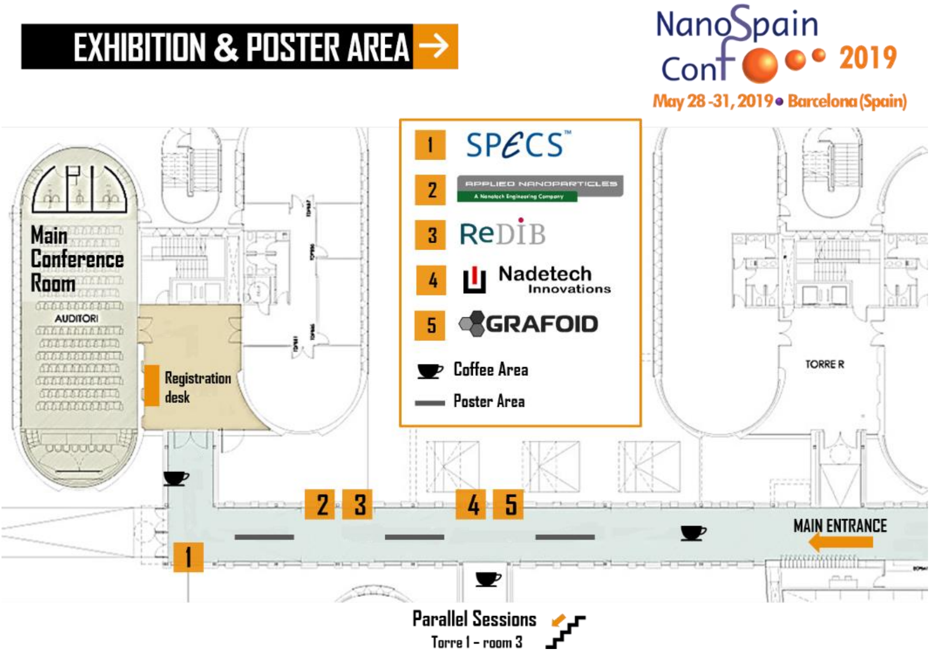

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Free-standing nanostructures at atomic scale: from growth mechanisms to local properties

Jordi Arbiol

ICREA & Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC & BIST
Barcelona, Catalonia, Spain
arbiol@icrea.cat

Technology at the nanoscale has become one of the main challenges in science as new physical effects appear and can be modulated at will. Materials for spintronics, electronics, optoelectronics, sensing, energy and quantum applications are taking advantage of the low dimensionality, improving their properties and opening a new range of applications. As developments in materials science are pushing to the size limits of physics and chemistry, there is a critical need for understanding the origin of these unique physical properties (optical and electronic) and relate them to the changes originated at the atomic scale, e.g.: linked to changes in (electronic) structure of the material.

In the present work, I will show how combining advanced electron microscopy imaging with related spectroscopies in an aberration corrected STEM will allow us to probe the elemental composition and electronic structure simultaneously with the optical properties in unprecedented spatial detail.

The talk will focus on several examples in advanced nanomaterials for optical, plasmonic, quantum and energy applications. In this way the latest results obtained by my group on direct Visualizing and modeling materials at atomic scale will help to understand their growth mechanisms (sometimes complex [1,2]) and also correlate their physical properties (electronic and photonic) at sub-nanometer with their atomic scale structure. The examples will cover a wide range of nanomaterials: quantum structures self-assembled in a nanowire: quantum wires (1D) [3] and quantum dots (0D) [4,5] and other complex nanowire-like morphologies for photonic and energy applications (LEDs, lasers, quantum computing, single photon emitters, water splitting cells, batteries) [7-13], nanomembranes and 2D sheets [8,14,15].

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Molecular engineering of polymersomes: design principles and applications

Giuseppe Battaglia[1,2,3,4,5]

[1]Department of Chemistry, [2]Institute for the Physics of Living Systems, [3]EPSRC/Jeol Centre for Liquid Phase Electron Microscopy, University College London, London, UK. [4]Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute for Science and Technology (BIST), Barcelona, Spain, [5]Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain

g.battaglia@ucl.ac.uk

Among the different biomimetic efforts, we have focussed our attention in possibly one of the few that encompasses polymerisation, compartmentalisation and positional self-assembly in the same unit; Polymersomes. These are vesicles formed by the self-assembly of amphiphilic block copolymers in water. Copolymers can be fully synthetic and/or derived from biomolecules and their sequence can be engineered to control both interactions with water and among each other. In analogy to natural vesicles (typically formed by phospholipids), polymersomes can house controlled aqueous volumes to create chemical potentials across the membranes. However, the macromolecular nature of the polymersome building blocks allows the design of vesicle membranes with control over their thickness, brush density, mechanical properties, and permeability. Furthermore, copolymers can be designed with tunable solubility, and hence, polymersomes can be made responsive to a large plethora of environmental stimuli such as pH, ionic strength, enzymatic degradation, hydrolysis, light, temperature, and many others.

We can summarise this into three steps process, at the molecular level (0.1-1nm) we can select appropriate molecules and use them as monomers for controlled polymerisation to form macromolecules with defined chemical signature to control supramolecular interactions (Macromolecular Engineering). These are then used to control the formation of larger structures (1-100nm) via a two-step processes (nucleation + growth) whose final topology is defined by the combination of the different supramolecular forces (Supramolecular Engineering). Polymersomes can be formed using either bottom-up or top- down approaches. The former involves a total solubilisation of the membrane-forming copolymers typically using organic solvents or exploiting pH, temperature or other stimuli that control the copolymer solubility. Once dissolved, the solution conditions are changed (e.g. solvent exchange of environmental changes) so to makes the copolymer amphiphilic and hence triggering the self-assembling. Polymersomes requires a minimum radius to be stable and hence a number of aggregates in order of thousands. This means that at the early stages of self-assembly, membrane forming copolymers nucleate into frustrated micelles and they further grow into enclosed vesicles. Similarly, as we hydrate a given amphiphilic copolymers, its internal structure evolve according to the different phase diagram discussed above and the final size and shape of the vesicles is given by the kinetics of hydration. We have been studying these kinetic for several years and learned how to control both bottom-up or top-down approaches to engineering the polymersome shape topology as showed in the Figure above. On a different level of complexity, we can also engineer the polymersome surface topology by combining different polymersome-forming copolymers and, in doing so, tuning the interaction between them. The resulting structures can be as simple as phase-separated bimodal or spinodal domains or more complex super-symmetric arrangements. Similarly, the same approach can be used to control the polymersome topography mixing different size copolymers and controlling line tension. Finally, the asymmetry of the polymersome can be further controlled pushing the phase separations to full coarsening (see the structure showed in Figure above).

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Dynamic Spray-Gun Deposition: a new way of conceiving the lego view for 2D and 1D nanomaterials

Paolo Bondavalli, Gregory Pognon, Lilia Quassym, Louiza Hamidouche, Clemence Rogier, Christophe Galindo,

Thales Research and Technology, 1Av. Fresnel, 91767 Palaseau, France
Paolo.bondavalli@thalesgroup.com

Abstract

This contribution deals with the fabrication of devices based on graphene based nanomaterials using dynamic spray-gun deposition method implemented through roll-to-roll. We used this technique to fabricate sensors, supercapacitors [1], flexible memories [1] and conformable Electro-Magnetic interference Shielding (EMI) layers. In the first case we exploited the nanostructuration of mixtures of graphene and carbon nanotubes (CNTs) to achieve electrodes for supercapacitors. Indeed the MWCNTs are used as sort of spacers to avoid the restacking of graphene. Thanks to that we can exploit the huge surface of graphene to store charges and at the same time we create channels between the layers allowing the rapid charge and discharge of the device. The use of high quality graphene (<5 layers) and MWCNTs, with a diameter of around 20nm, also improve the conductivity for the electrodes and allowed us obtaining an impressive specific power value of around 100kW/Kg using an industrially suitable technique and not only a lab based one [2-3]. The spray-gun deposition method has been also implemented in the fabrication of GO and CNFs Oxidized based memories. In this case we case spray nanomaterials water based suspensions on a flexible layer previously metallized. The total thickness is around 100nm. After contacting the top with metallic contacts we are able to achieve flexible non volatile memories simply applying a bias (<3V). These memories show bipolar behavior and have been cycled 10000 times. They constitute one of the first examples of information storage devices that can be fabricated using a roll-to-roll implementable method. Finally, we have achieved EMS architectures using nanostructuration of graphene, MWCNTs and carbon nanofibers between polymers layers in order to exploit the Maxwell-Wagner-Sillars effect to absorb X-band frequencies. Thanks to this nanostructuration we are able to trap the charges in sort of micro-capacitors created in the layers. This is a real breakthrough considering that usually heavy metal based layers are used and that in this case mm based conformable layers can be obtained opening the route for new kinds of applications. Also in this case the fabrication will be implemented by roll-to-roll fabrication. During the presentation we will show all the details on the first characterization of devices and we will show also perspectives for other potential field of applications.

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Interfacing functional molecules with 2D materials

E. Coronado

Instituto Ciencia Molecular, Univ. Valencia, C/ Catedrático José Beltrán 2, Paterna, Spain
Eugenio.coronado@uv.es

Graphene and other 2D materials have been a hot focus of interest in physics, chemistry and materials science. The emergence of van der Waals heterostructures formed by assembling two different monolayers of these materials through Van der Waals forces have opened new opportunities in this field. This concept can be further expanded by interfacing a layered 2D material with materials of other dimensionalities including 0D materials (molecules, nanoparticles,…), 1D materials (nanotubes, nanowires,…) and 3D materials, which can interact non only through VdW forces but also through covalent or ionic interactions [1].

Here I propose to create heterostructures based on functional molecules and 2D materials with the aim of tuning the properties of the "all surface" 2D material *via* an active control of the hybrid interface. This concept will provide an entire new class of stimuli-responsive molecular/2D heterostructures, which may be at the origin of a novel generation of hybrid materials and devices of direct application in highly topical fields like electronics, spintronics, molecular sensing and energy storage. I will focus in particular in heterostructures in which both or at least one of the two components are magnetic. This concept will be illustrated with two examples i) Chemically functionalized 2D magnetic metal-organic frameworks [2], and ii) Hybrid heterostructures based on spin crossover nanoparticles and 2D materials [3].

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Engineering personalized tissue implants: From 3D printing to bionic organs

Tal Dvir

Director of the Sagol Center for Regenerative Biotechnology
School of Molecular Cell Biology & Biotechnology,
Department of Materials Science and Engineering,
The Center for Nanoscience and Nanotechnology
Tel Aviv University. Tel Aviv, 69978, Israel
tdvir@tauex.tau.ac.il

Abstract

In this talk I will describe cutting-edge technologies for engineering functional tissues and organs, focusing on the design of new biomaterials mimicking the natural microenvironment, or releasing biofactors to promote stem cell recruitment and tissue protection. In addition, I will discuss the development of patient-specific materials and 3D-printing of personalized vascularized tissues and organs. Finally, I will show a new direction in tissue engineering, where, micro and nanoelectronics are integrated within engineered tissues to form cyborg tissues.

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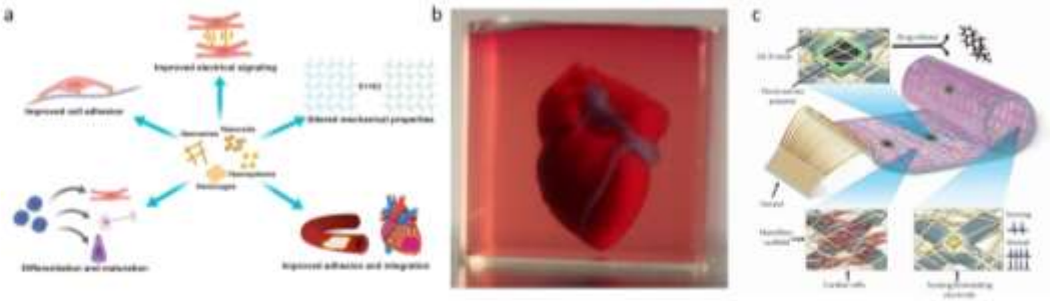
Figure



a. The use of gold nanoparticles in tissue engineering. b. 3D printing of a whole cellularized heart. c. Integration of nano and microelectronics with engineered tissue to provide control and regulation over its function.

Cascade of superconducting domes and magnetic order in charge neutral and ¼ filled magic angle bilayer graphene

Xiaobo Lu[1], Petr Stepanov[1], Wei Yang[1], Ming Xie[2], Aamir Mohammed Ali[1], Ipsita Das[1], Carles Urgell[1], Kenji Watanabe[3], Takashi Taniguchi[3], Guangyu Zhang[4], Adrian Bachtold[1], Allan MacDonald[2] and **Dmitri K. Efetov[1*]**

[1].ICFO - Institut de Ciencies Fotoniques, The Barcelona Institute of Science and Technol-ogy, Castelldefels, Barcelona, 08860, Spain
[2].Department of Physics, University of Texas at Austin, Austin TX 78712, USA
[3].National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan
[4].Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, 100190,China
Dmitri.Efetov@icfo.eu

Superconductivity often occurs close to symmetry broken parent states, in particular when doping magnetically ordered states. Flat bands in Moire lattices in twisted bilayer graphene have emerged as a rich and highly tuneable model platform, where superconducting domes were found close to correlated insulating states at ± ½ band filling, raising speculations of an unconventional pairing mechanism. Here we report on the fabrication of highly twist-angle homogeneous devices, which allow to resolve correlated states at all integer fillings ± ¼, ± ½, ± ¾ of the four-fold spin and valley degenerate Moire band, and a gapped insulating state at charge neutrality. We find an enhanced critical temperature of ~ 3 kelvin of the supercon-ducting dome close to – ½ filling, and strikingly we observe three new superconducting domes at much lower temperatures, when slightly doping the charge neutral point and the ±¼ filled correlated states. Interestingly, the weakly pronounced – ¼ correlated state shows a sharp hysteretic resistance enhancement when a perpendicular magnetic field above 3.6 tesla is applied, consistent with a field stabilized magnetically ordered state. Overall, our study shows that symmetry broken and superconducting states occur not only around half-filling, but are common across the entire Moire band, including charge neutrality. The co-existence of superconductivity and magnetic order in the – ¼ correlated states points to-wards a possible pairing mechanism. (in preparation)

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Figures

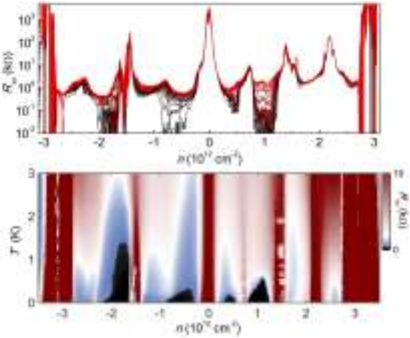

Figure 1: Superconductivity and correlated states in magic angle graphene.

Polymer Synthesis Enabled by Interfaces: Towards a world of organic 2D materials

Xinliang Feng

Center for Advancing Electronics Dresden & Faculty of Chemistry and Food Chemistry,
Technische Universitaet Dresden, Germany

Xinliang.feng@tu-dresden.de

Interface has been playing a key role in most “bottom-up” synthesis methods and is advantageous for directing the orientation of the molecules or precursors. By looking back at the history, the interfacial synthesis has been largely developed for the controlled polymer synthesis, which can be dated back to 1930s by Gee et al who achieved polymer monolayers at an air-water interface. Typically, the reactions at the interfaces between air-water (or gas-liquid), liquid-liquid, liquid-solid and gas-solid (or vacuum-solid) have been explored to offer paramount control over the morphology and the structure of polymers. While the synthetic linear polymers and cross-linked polymers are the main resultant structures in the historic interfacial polymer synthesis, it turns out only in recent years that a controlled 2D covalent reaction can take place if a finely designed interface is provided. A subsequent consequence of adsorption, nucleation, arrangement and polymerization of suitably designed precursors or intermediates, guided by a confined 2D geometry of interface, can yield a structurally well-defined, periodic organic 2D material such as 2D polymer.

In this lecture, we will present our recent efforts on the bottom-up synthetic approaches towards novel organic 2D materials with structural control at the atomic/molecular-level or at the meso-scale. First, 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 polymers at the air-water or liquid-liquid interfaces. The resulting 2D conjugated polymers exhibit single- to multi-layer feature, good local structural ordering and with a large size. The functional exploration of such 2D conjugated (coordination) polymers for the electrical, magnetic and mechanical properties, as well as serving as efficient electrocatalytic water splitting catalysts will be demonstrated. Next, 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 2D supramolecular polymers at liquid-liquid interface. Third, we will present the supramolecular approaches to synergistically 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. Finally, we will present a controlled synthesis of few-layer 2D polymer crystals on the water surface assisted by soft templates; we achieved micrometer-sized either horizontally or vertically grown 2D polyamide crystals by tailoring templating layers. The future perspective and outlook regarding the goal towards highly crystalline organic 2D materials will be also provided.

Novel materials for van der Waals heterostructures and advances in their nanofabrication

Roman Gorbachev

National Graphene Institute, University of Manchester, Oxford Road,
M13 9PL, Manchester, UK
roman@manchester.ac.uk

In the last years, a novel field has emerged which deals with structures and devices assembled layer-by-layer from various atomically thin crystals. These new multi-layer structures have proved to be extremely versatile, showing exceptional electronic and optical properties, new physics and new functionality. In this talk I will review recent progress and discuss new additions to the 2D material family, their fabrication and transport properties.

In this talk I will discuss the broad picture of 2D field development and current limiting factors in nanofabrication, such as crystal quality, contamination and environmental sensitivity of various 2D materials. I will introduce new techniques developed recently in Manchester that allow heterostructure assembly in ultra-high vacuum and compare properties of archetypal atomically thin crystals fabricated in different environments.

Lastly, I will focus on a novel material, indium monoselenide and present broad range of our results on its structural, optical and electronic properties. In-plane electronic transport, vertical resonant tunnelling experiments and PLE will be discussed as a measure of subband structure of the multilayer crystals can be mapped out, and shift of the subbands in transverse electric field measured experimentally through quantum confined Stark effect.

Figures

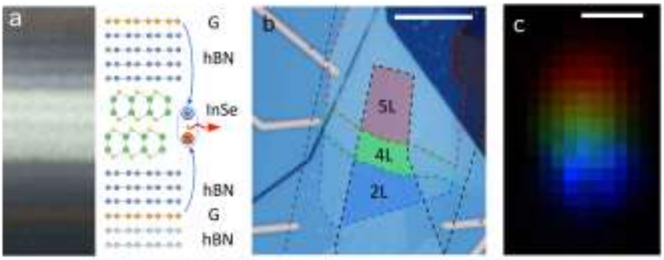

Figure 1: Example of LED heterostructure device based on indium selenide (a) Cross-sectional STEM image of the layer sequence, (b) optical micrograph with matching (c) electroluminescence map, where blue corresponds to the emission energy around 1.98 eV, green 1.50 eV and red 1.35 eV. Scale bars are 10 µm.

Engineered Quantum States in Graphene Nanoribbons

Oliver Gröning, Shiyong Wang, Qiang Sun, Pascal Ruffieux and Roman Fasel

Empa, Materials Science and Technology
Überlandstrasse 129
CH-8600 Dübendorf (Switzerland)
Oliver.groening@empa.ch

Graphene provides an ideal platform to create materials with diverse electronic properties by rational control of its nanoscale structure. Quantum confinement effects can be exploited in strictly planar 2D (e.g. porous graphen) or 1D (graphene nanoribbon GNR) graphene structures. However, in order to achieve well defined electronic properties with high electron motilities the nanostructures need to be synthetized with atomic precision.

In our presentation we will review the recent progress in the bottom-up synthesis of atomically precise graphene nanostructures from molecular precursors [1]. Very recently, it has been found theoretically that localized zero energy modes can be obtained at the junctions of topologically dissimilar graphene nanoribbons (GNR) [2]. We have experimentally realized such GNR junctions using on-surface synthesis, i.e. by the polymerization of molecular precursors rationally designed to yield the desired final GNR on single crystal surfaces. By creating well defined periodic sequences of these topological electronic modes, one-dimensional electronic bands can be created, which are described by the Su-Schrieffer-Heeger (SSH) Hamiltonian representing the dimerized atomic chain [3]. By manipulating the intra- and inter-cell coupling strength we could further create SSH analogs with different Chern number and therefore topological class. The topological class distinction is evidenced by presence, respectively absence of zero energy end states at the termini of the corresponding GNR or their junctions to structurally dissimilar GNRs.

We will discuss the concept of topological boundary states in GNR junctions and the creation of 1D SSH-type electronic bands by their periodic arrangement on a host GNR. The theoretical basis of attributing Z_2 topological invariants to these structures will be discussed. We then present the experimental synthesis of different structures exhibiting different topological classes. The structural characterization and atomic precision of these GNR was achieved by low-temperature scanning tunneling microscopy (STM) and high resolution non-contact atomic force microscopy (nc-AFM) [4]. The electronic properties are elucidated by scanning tunneling spectroscopy (STS), where we invoke the bulk-boundary correspondence to determine the topological properties.

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Guided Nanowire Optoelectronics

Ernesto Joselevich

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel
ernesto.joselevich@weizmann.ac.il

The large-scale assembly of NWs with controlled orientation on surfaces remains one challenge toward their integration into practical devices. During the last few years we reported the growth of perfectly aligned, millimeter-long, horizontal NWs of GaN [1], ZnO [2], ZnS [3], ZnSe [4], ZnTe [5], CdSe [6], CdS [7], $CsPbBr_3$ [8] and other materials, with controlled crystallographic orientations on different planes of sapphire [1-8], SiC [9], quartz [10], and spinel [11]. The growth directions and crystallographic orientation of the NWs are controlled by their epitaxial relationship with the substrate, as well as by a graphoepitaxial effect that guides their growth along surface steps and grooves. As a proof of concept for future applications, we demonstrated the massively parallel "self-integration" of NWs into circuits via guided growth [12]. Here we will show how guided nanowires with complex morphologies and heterostructures can be used for the bottom-up fabrication of nano-optoelectronic devices, including photodetectors [4-8,14] and photovoltaic cells [15].

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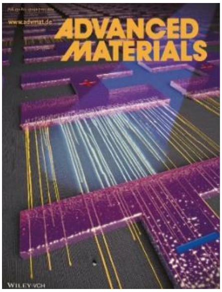

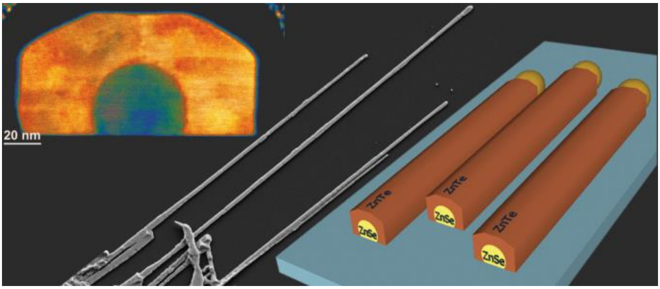

Electrochemical Exfoliation of 2D Materials for Composite and Energy Applications

Ian Kinloch

The University of Manchester, UK
Ian.Kinloch@manchester.ac.uk

The electrochemical exfoliation of 2D materials can produce flakes with morphologies that are difficult to achieve using other exfoliation techniques [1]. We have exfoliated graphene and TMD flakes using both reductive and oxidative routes, with a range of electrolytes including molten salts, deep eutectic salts, organic and aqueous. Anodic exfoliation of graphite tends to produce material that is more oxidised, but the oxygen content can be reduced using metal salts [2] or by separating the intercalation and oxidation reactions [3]. Whilst cathodic exfoliation produces more "pristine" flakes albeit at slower rates and also gives the opportunity for in-situ functionalisation [4].

Energy storage and composites [5] are both very promising applications for graphene materials and the talk will discussion the design rules these applications, highlighting how the morphology [6] and hence production route of the material [7] is crucial in obtaining the best properties

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Development of nanomedicines for boron neutron capture therapy

Jordi Llop, Vanessa Gómez-Vallejo, Unai Cossío, Irene J. Feiner, Marcos Navascuez, Krishna R. Pulagam.

Radiochemistry and Nuclear Imaging Group, CIC biomaGUNE, Paseo Miramon 182, San Sebastian, Spain
jllop@cicbiomagune.es

Boron Neutron Capture Therapy (BNCT) is a binary approach to cancer therapy based on the ability of Boron-10 (^{10}B) to capture thermal neutrons, which results in the $^{10}B(n, \alpha, \gamma)^{7}Li$ nuclear reaction. Alpha particles and ^{7}Li recoil ions have high linear energy transfer properties and path lengths in the range of the diameter of a single cell. Hence, if cancer cells selectively take up a sufficient amount of ^{10}B and are irradiated with thermal neutrons, the alpha particles and ^{7}Li ions result in cellular damage and trigger cell death, while sparing healthy surrounding tissue.

During decades, different molecular modalities have been proposed as BCNT drug candidates, including boronated carbohydrates, amino acids, peptides, nucleic acids and immunoconjugates [1]. However, and in spite of huge efforts, only two compounds, i.e. sodium borocaptate (BSH) and p-boronophenylalanine (BPA), are currently approved for clinical trials, and they show low specificity. The recent emergence of nanotechnology has opened new avenues to achieve preferential delivery of boron atoms in tumours taking advantage of the well-known enhanced permeability and retention (EPR) effect, which is based on the presence of leaky vasculature and deficient lymphatic drainage in the vicinity of tumours. This, ultimately, results in a passive accumulation of non-targeted nanosized materials in tumour tissue after intravenous administration. In the last years, a plethora of nanostructured materials have been assayed as boron delivery agents, including liposomes, carbon nanotubes, boron nitride nanotubes, magnetic nanoparticles, boron carbide nanoparticles, borosilicates and functionalized gold nanoparticles.

Here, we will present our recent advances in the development of different boron-rich nanosized materials that could be used for BNCT, including functionalized gold nanoparticles and micelles. The preparation methods will be described and discussed. Additionally, radiolabelling strategies to assess the capacity of the novel nanosystems to reach different tumor types by means of in vivo positron emission tomography will be presented. In vivo data could not only predict the therapeutic efficacy of novel BNCT agents, but also identify the optimal time window for neutron irradiation application.

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Figures

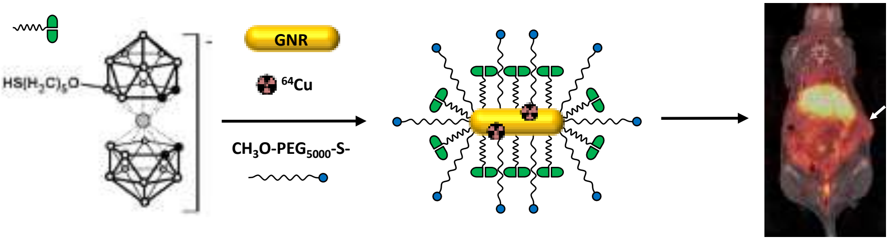

Figure 1: Schematic representation of the synthesis/radiolabelling of boron-rich gold nanorods (GNRs) and their in vivo evaluation in a mouse model using Positron Emission Tomography.

Nanomaterials for 2, 3, 4D printing

Shlomo Magdassi

The Hebrew University of Jerusalem, Institute of Chemistry, Jerusalem, Israel
Magdassi@mail.huji.ac.il

Abstract

Additive manufacturing brings new opportunities in fabrication processes, which are based on printing. Nanomaterails such as metal nanoparticles and carbon nanotubes enable printing beyond color, towards fabrication of functional devices. The synthesis and formulations of nanoparticles and inks will be presented, along with their utilization in printed devices, responsive and 3D objects. New approaches for electrical circuits for printed electronics will be presented, as well as new materials and processes for 3D and 4D printing. Utilization of 3D and 4D printing technologies for fabrication of objects composed of ceramics, MOFs, shape memory polymers, elastomers and hydrogels will be demonstrated, for applications such as soft robotics, drug delivery systems and Internet of Things (IoT).

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Highly-controlled graphene functionalization as a platform for robust nano-bio-hybrid interfaces

José A. Martín-Gago

[1] Institute of Materials Science of Madrid (ICMM-CSIC), Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain
gago@icmm.csic.es

Although pristine graphene is one of the most relevant materials this decade, several important shortcomings must be overcome before it can step from fundamental physics to applied technology. In particular, its extreme chemical inertness and the absence of an electronic band-gap present important limitations to its use as an active element in electronic devices and hybrid structures. Thus, technologically useful and robust graphene-based interfaces for nano-bio-hybrid devices require highly selective, stable and covalently bonded functionalities on the graphene surface, but in order to be effective and competitive they must essentially retain the electronic properties of the pristine graphene surface. There have been many attempts to modify graphene via non-destructive methodologies that aim to preserve its extraordinary properties and incorporate added value. In this talk, we describe a relatively straightforward route to the covalent chemical functionalization of graphene sheets, with any amino containing molecules, as anchoring group. [1]. We employ a recently reported and patented strategy [3] for the selective functionalization of graphene through the controlled formation of atomic vacancies (Fig. 1a), obtaining a graphene surface uniformly covered with a covalently bound spacer molecule that is formed from the spontaneous bonding of, for example, *p*-aminothiophenol (pATP) molecules at the vacancies. The result is a controlled decoration of the graphene surface with active thiol moieties, which can subsequently be directly used to bind diverse nanoarchitectures to graphene. We have used this strategy to covalently couple two systems of broad interest: gold nanoparticles (Au-NPs) [3] and thiol-modified nucleic acid aptamers (Fig. 1b). This work opens the door to the integration of high-quality graphene layers in technological platforms for plasmonics, biosensing or advanced field-effect transistor devices.

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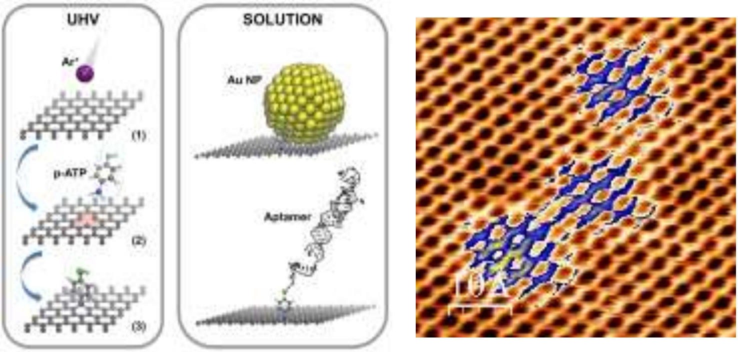

Figure 1: Left: Schematic illustration of the two-step functionalization process. Right: STM image with atomic resolution of graphene functionalized with aminophenol molecules

The use of algal photosynthesis as a sensor of bioavailable silver from nanomaterials at complex biological interfaces

Patricia Salas[1,2], Niksa Odzak[3], Yolanda Echegoyen[4], Ralf Kägi[3], M.Carmen Sancho[1] and **Enrique Navarro[1]**

1. Pyrenean Institute of Ecology-CSIC, Av. Montañana 1005, Zaragoza 50059, Spain
2. Sonea Ingenieria y Medio Ambiente S.L., P.Tec. WALQA, Ctra. Zaragoza N330 Km. 566, Huesca, Spain
3. Eawag, Überlandstrasse 133, Dübendorf 8600, Switzerland
4. Dept. of Experimental and Social Sciences Teaching, University of Valencia, Avd. Tarongers 4, Valencia 46022, Spain

enrique.navarro@ipe.csic.es

Silver nanoparticles –AgNP- are among the most used nanomaterials in consumer products.Their applications relates to the biocidal activity of the silver ions (soluble Ag) released from nanoparticles and nanostructured surfaces. However, it is difficult to assess the Ag readily bioavailable from silver nanoparticles at biological interfaces (i.e. nanoparticles interacting with algal cells). Because the fast biological uptake of silver by cells, traditional methods for assessing dissolved –bioavailable- silver usually understimates the amount of active silver that would be delivered once in contact with living cells. This exposure scenario becomes more complex if coatings, modulating the release of dissolved silver, are involved.

The use of the algal photosynthesis as a short-term sensor of bioavailable silver may support traditional analytical methods (see Figure 1), providing a more complete picture at biological interfaces. This approach has been early developed in 2008[1], being later applied to differently coated AgNPs[2] and nanostructured surfaces[3], and finally being applied in the improvement of marketed products[4]. The use of algal photosynthesis allowed for for understanding the role of different chemicals used as coatings, and the role played by differently sized shells in the amount of bioavailable Ag.

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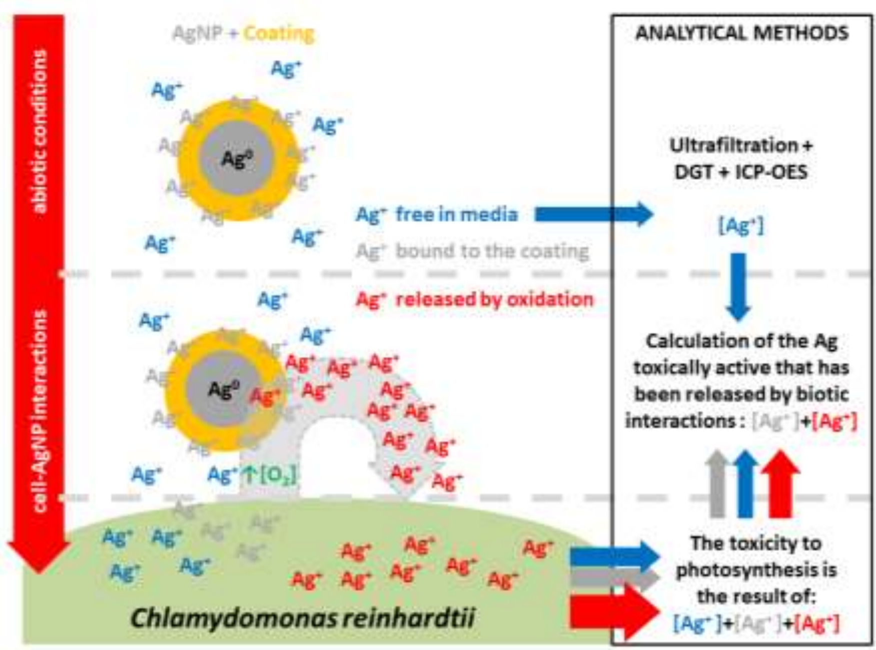

Figure 1: Conceptual model, explaining how the AgNPs measured toxicity on the photosynthesis of *C. reinhardtii* allows us to estimate the amount of ionic Ag (Ag^+) released under biotic conditions (i.e. interactions between photosynthetically active algal cells and AgNPs in suspension). Methods used under abiotic conditions understimate the amount of bioavailable Ag at the AgNP-cell interfaces. Combining traditional methods (i.e. Diffusive Gradients in Thin Films –DGT; ICP-OES, etc…) with the information provided by the photosynthesis, there is a more complete picture of the processes involved in the delivery of bioavailable Ag at the biological intefaces.

The Chiral Induced Spin Selectivity Effect (CISS)

Yossi Paltiel

Applied Physics Department and the Center for Nano science and Nanotechnology, Hebrew University, Jerusalem 91904, Israel
Paltiel@mail.huji.ac.il

Abstract

Living organisms rely on chiral molecules, such as nucleic acids and proteins. A chiral molecule is not superimposable on its mirror image, also known as its enantiomer, just like our right hand cannot be superimposed on our left hand. Organisms contain only one enantiomeric form of a molecule, a selectivity that has prevailed through evolution. We claim that the chiral induced spin selectivity (CISS) effect can explain why enantiomeric purity might provide an advantage in biology. CISS is an electronic phenomenon in which electron transmission through chiral molecules depends on the direction of the electron spin, a quantum mechanical property associated with its magnetic moment. Thus charge displacement and transmission in chiral molecules generates a spin-polarized electron distribution. This effect; enhance electron transfer in proteins, enable nano metric charge separation, and explain biorecognition [1].

From the application point, by utilizing the CISS effect we realized a magnet less spin based, nano magnetic optical and electrical memory [2,3,4,5]. The presented technology has the potential to overcome the limitations of other magnetic-based memory technologies to allow fabricating inexpensive, high-density universal and embedded memory-on-chip devices [6] (figure 1).

Using similar effects, we have demonstrated that magnetic ferromagnetic surfaces can supply a simple generic way to separate between two enantiomers. Achieving enantiopurity is of great importance to many industrial fields. This enantiospecific interaction is controlled by surface magnetization and the chirality of oligopeptides, oligonucleotides, and amino acids [7].

In my talk I will present the CISS effect and its importance, both for applications and basic science. I will also point to open questions regarding the CISS.

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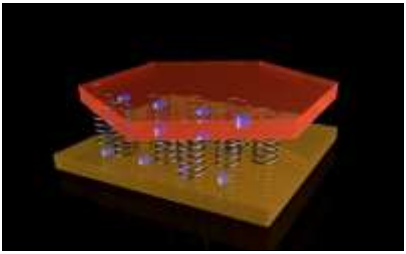
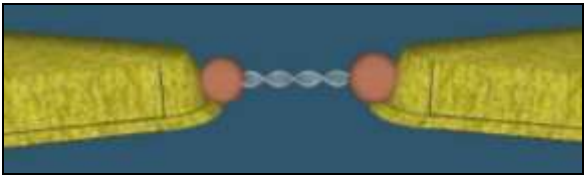


Figure 1: Usung the CISS effect a single ferromagnetic nanoplatelet, along with Au contacts and chiral molecules, is sufficient to function as a memory device.

Novel DNA-Based Molecules and Their Charge Transport Properties

Danny Porath

Institute of Chemistry and Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, 91904 Israel
danny.porath@mail.huji.ac.il



Charge transport through molecular structures is interesting both scientifically and technologically. To date, DNA is the only type of polymer that transports significant currents over distances of more than a few nanometers in individual molecules. Nevertheless and in spite of large efforts to elucidate the charge transport mechanism through DNA a satisfying characterization and mechanistic description has not been provided yet. For molecular electronics, DNA derivatives are by far more promising than native DNA due to their improved charge-transport properties.

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

In collaboration with the Kotlyar group, We were also able to synthesize and measure long (hundreds of nanometers) DNA–based derivatives that transport significant currents when deposited on hard substrates. Among the molecules, metal containing DNA, which is true metal-organic hybrid, a smooth and thin metal coated DNA and G-quadruplex DNA.

Step by step we improve the synthesized constructs and the measurement methods of single DNA-based molecules. I will present new and surprising results on dsDNA molecules. I will present new DNA-based molecules and report on our measurements of their properties.

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The use of metal oxide nanoparticles as third generation immunotherapy: Phenotypic changes follow changes in the chemical potential.

Victor Puntes

Design and Pharmacokinetics of Nanoparticles, CIBBIM-Nanomedicine, Vall d'Hebron Insitute of Research (VHIR), Barcelona, Spain
Institut Català de Nanociència i Nanotecnologia (ICN2), (CERCA-CSIC-UAB) 08193 Bellaterra, Spain;
Institut Català de Recerca i Estudis Avançats, (ICREA), P. Lluis Companys 23, 08010 Barcelona, Spain

victor.puntes@vhir.org

Recently, nanomaterials have been proposed for use in the treatment of certain cancers and other human diseases. Among those, Cerium oxide nanoparticles (CeO2NCs) have emerged in biomedical applications due to their multienzymatic character that buffers oxidative stress and Reactive OxygenSpecies (ROS). This material has shown to have both anti-inflammatory and antitumoral behaviour [1]. Previous studies have shown that CeONP is cytotoxic to cancer cells, inducing oxidative stress and causing lipid peroxidation and cell membrane leakage. It is also reported to protect normal cells but not cancer cells from ROS damage. This may be attributed to cancer cells having a more acidic cytosolic pH than normal cells because of higher glycolysis and significantly higher production of lactate. As previously mentioned, in acidic conditions, the antioxidant ability of CeONP is lost and it behaves as a strong oxidant, which may facilitate the oxidation of intracellular and extracellular components to induce cell apoptosis. Besides, more recently superparamagnetic iron oxide (magnetite) NPs have been also shown to play a role with oxidative stress altering the tumour microenvironment, inducing macrophages M1 polarization and resulting into benefitial anti-tumoral effects [2].

It is well known that the ROS can drive both the initial development and progression of cancer, as well as down regulate antioxidant enzymes that normally combat radical production. In cancer, ROS account for its genomic instability, resistance to apoptosis, proliferation, and angiogenesis. Importantly, ROS trigger cancer cell invasion as well as extravasation into distant metastasis sites. In normal, healthy cells, the cellular levels of ROS are tightly controlled. The ability to modulate the redox status of cells has applications in cancer where ROS levels have become deregulated or are altered by treatment. Some studies have shown CeO2NCs to possess innate cytotoxicity to cancer cells, anti-invasive properties, and the ability to sensitize cancer cells to radiation-induced cell death (due to the generation of free radicals by the ionizing radiation), while protecting the surrounding normal tissues. This could be reproduced with Fe3O4 inducing the generation of free radicals in a Fenton like raction and the CeO2 amplifying it.

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Internet of functions in hybrid supramolecular nanomaterials

Paolo Samorì

ISIS, University of Strasbourg & CNRS, 8 allée Gaspard Monge, 67000 Strasbourg, France
samori@unistra.fr

Nowadays, Internet of Things is becoming a leitmotiv in our daily life, the latter being characterized by interconnected macroscopic tools and technologies thereof operating 24/7. On the nanoscale, one among the greatest challenges in chemistry consists in the development of artificial Complex Chemical Systems with functions that are getting more and more sophisticated and interconnected among each other.

In my lecture I will review our endeavor on the use of supramolecular chemistry approaches towards the development of multicomponent assemblies comprising low dimensional nanostructures. In particular I will discuss our recent results on:

1) imparting multiple functions to organic electronic devices via the combination of carbon-based nanomaterials, especially organic semiconductors, with photochromic molecules (diarylethenes or azobenzenes) in order to realize smart, high-performing and light-sensitive (opto)electronic devices [1] as well as flexible non-volatile optical memory thin-film transistor device with over 256 distinct levels.[2]

2) interfacing molecular science with 2D materials, by mastering covalent and non-covalent approaches,[3] in order to tune of the dynamic physical and chemical properties of 2D materials, by imparting them novel functions,[4] with the ultimate goal of generating responsive thus multifunctional hetero-structures.[5]

3) the tailoring of low-dimensional nanostructures chemically functionalized by the receptors of the target analytes and on the use of these hybrid assemblies to fabricate chemical sensors (e.g. humidity) combining high sensitivity, selectivity, response time and reversibility.[6] Finally, I will describe how the same approaches can be exploited to realize highly sensitive pressure sensors which can monitor heartbeats, thus holding great potential for their integration in medical diagnostic devices or sport apparatus.[7]

Our approaches provide a glimpse on the chemist's toolbox to generate multifunctional hybrid materials based with ad-hoc properties to address societal needs in electronics, sensing and energy applications.

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Nanomotors: Active nanoparticles that move, respond to stimuli, sense, clean, and transport drugs efficiently

Samuel Sánchez

[1]Smart Nano-Bio-Devices Group, Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute for Science and Technology (BIST), Barcelona, Spain
[2] Catalan Institute for Research and Advanced Studies (ICREA), Barcelona, Spain
ssanchez@ibecbarcelona.eu

Inspired by nature, researchers have been exploring the possibility to mimic the rich multifunctionality of molecular motors, cells and other microorganisms capable of moving, interacting, communicating and cooperate in complex biological environments. Artificial nanomotors are active particles that constantly consume energy from their surroundings to engage in self-propulsion and mimic biological micro-swimmers in many ways.

One of the challenges in nanotechnology is to engineer smart systems which can respond to stimuli and act accordingly to a given task. Among other interesting applications, the design of nanovehicles which can eventually be applied in vivo for medical purposes for imaging and/or directed drug delivery is of outmost importance. Major advances have been demonstrated towards that end, however, questions like "how to swim at the nanoscale, how to achieve motion control and how to image these nanobots" need to be properly addressed.

Here, I will present our recent developments in the field of nanomotors that can autonomously swim and perform complex tasks in vitro [1]. Our "bots" combine the best from the two worlds: biology (enzymes, single cells and tissues) and (nano)technology (nanoparticles, 3D Bioprinting) providing remote control, guidance and actuation. We demonstrated the efficient transport and the enhanced release of drugs into cancer cells [2] and spheroids [3], sensing [4] capabilities and their use in water remediation [5].

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Figures

Figure 1: Fundamental studies and applications of self-powered nanomotors (covers from references 5 and 1 b)

Transport in Low-Dimensional Systems from Theory and Experiment: Two-Probe Scanning Spectroscopy on Ge(001)-c(4x2) and Graphene Nanoribbons

Daniel Sánchez-Portal
Centro de Física de Materiales CSIC-UPV/EHU and DIPC, Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain
daniel.sanchez@ehu.eus

With the miniaturization of electronic circuits into the single-atom level, methods based on scanning probe microscopy are becoming instrumental to characterize electron transport properties of relevant devices. Here I will present two joint theoretical and experimental studies of electronic transport in low-dimensional systems.

Firstly, I will focus on the electronic transport along the anisotropic Ge(001)-c(4x2) surface with the use of two-probe scanning tunneling spectroscopy (2P-STS) and first-principles transport calculations [1]. We have introduced a method for the determination of the transconductance in our two-probe experimental setup and demonstrated how it captures energy-resolved information about electronic transport through the unoccupied surface states. The sequential opening of two transport channels within the quasi-one-dimensional Ge dimer rows in the surface gives rise to two distinct resonances in the transconductance spectroscopic signal, consistent with phase-coherence lengths of up to 50 nm and anisotropic electron propagation. Theoretical results from ballistic transport simulations allow correlating the observed resonances with different features in the surface band structure (see Figure 1 below).

Secondly, I will present results for the electronic and transport properties of simple devices based on graphene nanoribbons (GNRs) [2] and 7-armchair-GNRs doped with boron [3,4], comparing our findings in the latter case with detailed STS experiments.

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Figures

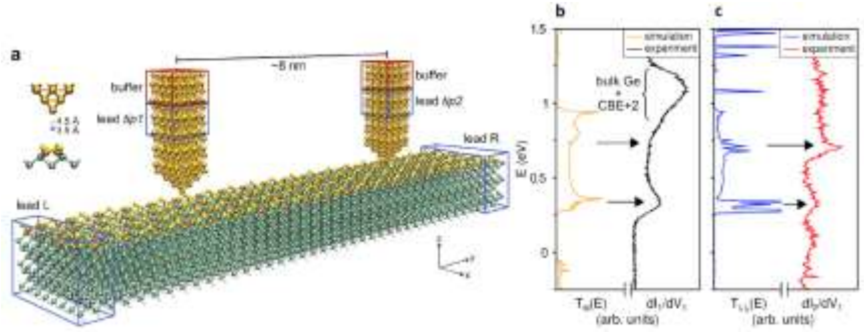

Figure 1: (**a**) Scheme of our 4-terminal computational setup. Computations were performed with the SIESTA/TranSIESTA package. (**b**) Comparison between the experimental dI_1/dV_1 spectrum and the calculated surface-to-tip transmission at zero bias for D=4.5 Å (single-tip setup). (**c**) Comparison between the experimental dI_2/dV_1 spectrum and the tip-to-tip transmission function calculated for $D_1=D_2=3.5$ Å with the setup represented in panel **a**. In all calculations the Ge slab valence band edge has been used as a common energy reference.

Photocurrent properties of junctions with single PbSe quantum dots

Yoram Selzer, Iftach Ilsar

Tel Aviv University, Tel Aviv, Israel
selzer@tauex.tau.ac.il

Understanding charge transport in photoexcited coloidal quantum dot (QD) solids is key to their applications in optoelectronic devices. Despite recent progress towards this end, the physics which governs the photoconductance properties of these structures is surprisingly still unclear and elusive.

One possible route to facilitate better understanding of these systems is, instead of performing photoconductance measurements of large ensemble of QDs, to measure individual QDs located within nano-scale gaps between two metal leads. While the conductance properties of such junctions has been studied quite extensively, the study of their photoconductance properties is surprisingly very scarce.

Here I will report of low-temperature photocurrent measurements of nano-scale junctions with single PbSe QDs.

Several novel effects in the dc-current photoresponse of these junctions will be discussed such as the destruction of photocurrent at specific voltage bias values and photo-induced gating.

Analysis of their time-resolved response as well as their noise properties reveals further information on the mechanisms that govern their photoconductance behavior.

The presented results are argued to be complimentary to the information gained by photoluminescence measurements of individual QDs.

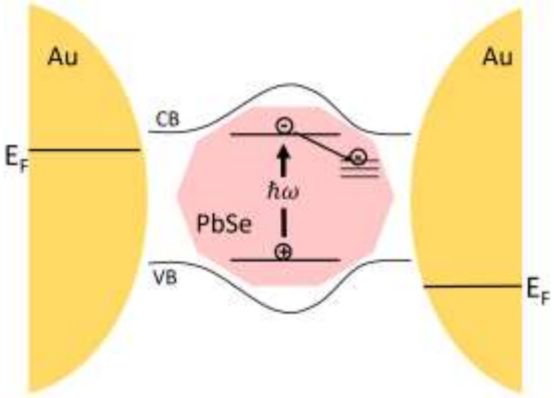

Figure 1: Schematics of a PbSe quantum dot within a nano-scale junction with Au leads. Also shown are the energy levels that are relevant for the interpretation of the photoconductance properties of such a junction.

Nanophotonics – where do the photons go?

Niek F. van Hulst
1 ICFO – the Institute of Photonic Sciences, Castelldefels, Barcelona
2 ICREA – Institució Catalana de Recerca i Estudis Avançats, Barcelona
Niek.vanHulst@icfo.eu

Optical antennas, with their ultra-confined, sub-diffraction-limited mode volumes, offer huge coupling strengths (in the 1−100 meV range) when coupled to single quantum emitters, such as molecules, NV-centres and other defects emitters. The strong coupling makes nano-antenna cavities desirable for applications in bright, fast-emitting photon sources, and ultrasensitive detection of biomolecules. Here we apply both deterministic scanning probe [1, 2] and stochastic localisation [3] mapping of the nanoscale plasmon-molecule interaction, to enhance sensitivity, resolution, rates and to optimize the coupling strength and ultrafast interaction. By scanning the antenna we achieve coupling up to 100 GHz [2], 1000-fold enhancement on biomolecules [4], detection of molecules which are otherwise invisible, and local maps of defect emitters in 2D-materials with 20 nm spatial response. In a complementary approach, using stochastic localisation, analogous to super-resolution microscopy, we show that the offset in far field super-localised position of molecule-antenna system is a direct indication for the coupling strength. By statistical single-molecule data analysis, we effectively isolate the strong interaction cases [3].

Plasmonic antennas are lossy and subject to heating upon excitation. In fact, hot electrons in noble metals are attracting attention for applications in thermoelectric devices, broadband photodetectors, efficient solar cells and even plasmon-enhanced photochemistry. Here, we present scanning ultrafast thermo-modulation microscopy, to map and track spatial hot-electron diffusion in a plasmonic gold layer with 20 nm spatial resolution. The spatio-temporal imaging reveals a transition from a very fast initial diffusion within the first picoseconds to a 100-fold slower diffusion at later times [9].

I will conclude with an outlook of the challenges ahead and the perspectives of addressing coupled systems in real nano-space and on femtosecond timescale..

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Invited contributions

Towards a biosensing platform based on graphene field-effect transistors

Pedro Alpuim[1,2], T. Domingues, J. Rafaela Guerreiro[1], E. Fernandes, P. Cabral, A. Ipatov[1], D. Y. Petrovykh[1], J. Borme[1]

[1]INL-International Iberian Nanotechnology Laboratory, 4715-330, Braga, Portugal
[2]CFUM-Center of Physics of the University of Minho, 4710-057, Braga, Portugal
pedro.alpuim.us@inl.int

Miniaturized biosensing analytical devices are essential tools for the successful development of point-of-care testing, for so-called "intelligent factories" (Industry 4.0), and for automated environmental monitoring, due to the possibility of integration, automation, and connection between analytical devices. We propose the development of a miniaturized biosensing device based on liquid-gate graphene field-effect transistors (GFETs) comprising 3 modules: target extraction and purification, isothermal target amplification, and detection. The sensor readout consists of a home-made electronic platform, with the size of a credit card, to ensure portability (Fig. 1E). Here, we report on the detection module: the GFET sensor chip and a PDMS flow cell, fitting the sensor layout, are assembled and then inserted in the portable platform (Fig. 1C,D). This system, connected to a syringe pump and a multiposition valve, allows for automation, improving the precision over manually operated ones [1]. We focus on the detection of two molecular targets: a 30-nucleotides long single stranded DNA that is part of the genome of a Port wine grape variety, and an antigen that is a biomarker of the hemorrhagic transformation of ischemic stroke, matrix metallopeptidase 9 (MMP-9). For the target detection the GFET channel is functionalized with a molecular probe – a DNA sequence, complementary to the DNA target, or an anti-MMP-9 antibody, specific to MMP-9, respectively. Different linkers (PBSE, FSC and AO succinimidyl ester) in distinct solvents (ethanol, DMSO, and DMF) were tested and the highest surface coverage was obtained using PBSE in DMF, giving ~10^{13} molecules/cm^2 for DNA and ~10^{12} antibodies/cm^2 for anti-MMP-9 probe concentration. Each modification step was monitored by measuring 10 transfer curves and, from the last 3 curves, computing the average of the gate voltage values at which maximal channel resistance is observed (V_{Dirac}). The observed shifts in V_{Dirac} are consistent with a mechanism of local gating of graphene by charged molecules [3]. Target DNA was detected down to 1 aM, with a saturation attained at 100 fM and sensitivity to SNP, and MMP9 was detected in a range from 0.01 up to 10 ng/mL. These results show that graphene liquid-gate transistor sensors, with high sensitivity and low cost, are a promising technology for next generation lab-on-a-chip devices. Moreover our functionalization strategy can be easily transferred to a broad range of probes for the detection of biomarkers in many different fields.

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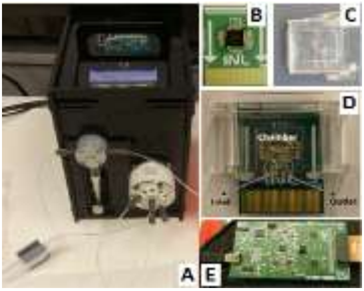

Figure 1: Detection module, A) Flow injection system; B) multi GFET chip; C) PDMS chamber; D) PDMS/GFET chip; E) platform readout.

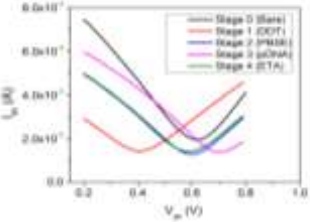

Figure 2: Transfer curves after each stage of GFET channel functionalization

On the quantification of heteroatoms in carbon nanotubes at bulk and local scale

Paola Ayala

University of Vienna, Boltzmanngasse 5, Vienna, Austria
paola.ayala@univie.ac.at

Abstract

Various functionalization methods for carbon nanotubes have been proposed over several years now. [1] Among those, substitutional doping and intercalation are methods that can be done with atoms of one same element distributed within the bulk carbon nanotube sample or incorporated as part of the tubular structure. [2] Their presence induces changes in the physical properties of the materials that are very desirable for applications but to make this effective, a proper understanding of the heteroatom content and distribution should be controlled. In a different context, the advances in sorting and purification of single-walled carbon nanotubes (SWCNTs) of the last years opened several possibilities for their applicability. SWCNTs with on-wall functionalization are nowadays produced with different methods. However, sorting and purification of functionalized materials in general has been scarcely explored. Therefore the understanding how the energies of charge carriers and lattice vibrations are modified, among other effects due to the presence of heteroatoms and defects is still elusive despite many years of worldwide efforts. I will show our progress on establishing the prerequisites for studying the rich low-dimensional physics of substitutionally doped SWCNTs as an example. [3] It will be discussed how metallicity-sorting combined with high energy spectroscopy techniques can nicely disentangle the characteristic density of states of doped SWCNTs with different doping levels unambiguously. We will discuss the changes in the site selective electronic structure of other various examples of functionalized SWCNTs. [2-4]

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Adding ECO on aquatic toxicity studies conducted with nanoparticicles. A case study of nanoparticles of TiO2 on Daphnia magna life-history performance across food ratios

Carlos Barata, Bruno Campos

IDAEA-CSIC, Jordi Girona 18 , 08034 Barcelona, Spain.
cbmqam@cid.csic.es

Abstract

Despite the huge amount of studies that have addressed the toxicity of nanoparticles across species and environmental conditions, few of them have truly used ecological relevant exposure scenario. The use of unrealistic exposure scenarios may aggravate the estimated environmental risks of nanoparticles. This is the case for many nanoparticle forms that despite having low toxicity to organisms aggregated in aqueous solutions and as such may facilitated the sedimentation of edible particles and hence may dramatically affect those organisms that feed on those particles. In this talk we present results on the extent to which different forms of nanoparticles of titanium dioxide (nano-TiO2) aggregated with microalgae, decreased food levels and hence impaired growth, reproduction and fitness of *Daphnia magna* individuals [1]. Treatments included three different types of nano-TiO2 differing in their coating or cristalline structure but of similar primary size (20 nm) plus a micron-sized bulk material, two exposure levels (1, 10 mg/l) and two food ration levels of the microalgae *Chlorella vulgaris* that included an non limiting (1.5 µg C/ml) and a limiting one (0.3 µg C/L). Effects were assessed using standardized chronic tests and assays that maximized food depletion in the water column under semi-static and re-suspension conditions. Results indicated that the high ion levels in culture medium lead to the aggregation of nanoparticles followed by particle destabilization. Nanoparticle aggregates interacted with the algae cells, forming clusters. Large TiO2-algae agglomerates settled readily depleting dramatically the concentration of edible food for *D. magna.* At limiting food ratios food depletion by nanoparticle aggregation had dramatic effects on reproduction and fitness of exposed *D. magna* at 1 mg/L irrespectively of the particle form. At high food rations effects were only observed for one of the nano-TiO2, P25, at high exposure levels (10 mg/l) under both semi-static and particle re-suspension conditions, which suggest that P25 effects were mediated by clogging the gut and hence diminishing food acquisition. These results indicate that nano-TiO2 may affect the transfer of energy throughout the planktonic aquatic food webs increasing the settlement of edible particles from the water column..

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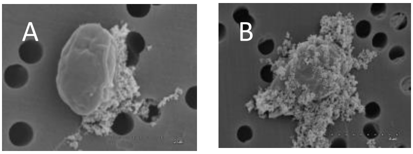

Figure 1: SEM Images of algae cells in the presence of 1 mg/L (A) and 10 mg/L (B) of P25-TiO2 at high food levels.

Point-like defects in transition metal dichalcogenides characterized by SPM simulations

Blanca Biel

Dep. of Atomic, Molecular and Nuclear Physics, Faculty of Science, University of Granada, 18071 Granada, Spain
biel@ugr.es

Defects are frequently present in 2D materials, and as such have been extensively studied on suspended samples. However, to describe realistically their electronic properties and their SPM characterization, simulations need to take into account the presence of the metallic substrates commonly employed during the growth and the characterization processes, which might substantially alter the electronic structure of the 2D material.

The interaction between metallic substrates and pristine transition metal dichalcogenides (TMDs) can greatly vary depending on the metal [1]. In this work, we have studied the interaction of several point-like defects in TMDs monolayers with underneath Ir(111) and Au(111) substrates by means of DFT calculations and SPM simulations, revealing a notably different behavior depending on the metallic substrate considered. The hybridization of the S states with those of the Ir(111) substrate induces a shift of ~1 eV of the MoS_2 states towards the valence band and a large broadening of the defect states [2]. The interaction with a gold substrate is much weaker, as confirmed by experimental data [3], leading to sharper defect states (Fig.1), much more similar to those found for freestanding MoS_2.

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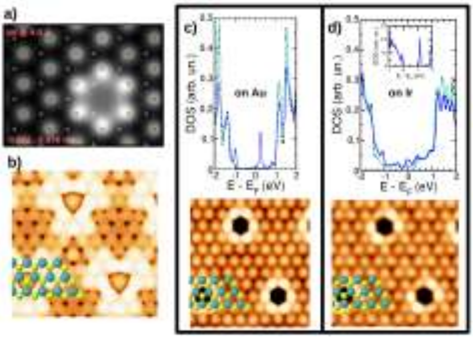

Figure 1: Left panel: AFM (a) and STM at -0.1 V (b) images of a S vacancy at the top layer for freestanding MoS_2. Right panel: LDOS of top S atoms close (blue) and far (cyan) of the defect site and STM images at V = -0.1 V for a top S vacancy in epitaxial MoS_2/Au(111) (c) and MoS_2/Ir(111) (d). Inset in d): LDOS of a top S vacancy in freestanding MoS_2.

Environmental impact of metal-bearing nanoparticles and graphene family nanomaterials

Miren P. Cajaraville

CBET Research Group, Dept. Zoology and Animal Cell Biology; Faculty of Science and Technology and Research Centre for Experimental Marine Biology and Biotechnology PiE, University of the Basque Country UPV/EHU, Basque Country, Spain
Contact email: mirenp.cajaraville@ehu.eus

The development of Nanotechnology and Nanoscience has resulted in the synthesis of innovative nanomaterials (NMs) with unique properties and the appearance of new consumer products useful for a variety of biomedical, textile, cosmetic, food and other industrial applications. However, the increased use of NMs could pose a risk for the environment and human health. NMs can interact with biological systems but there is still limited information on their fate, distribution and toxicity to living organisms. Among NMs, metal and metal oxide nanoparticles (NPs) are already present in thousands of consumer products. Similarly, carbon-based NMs such as graphene and its derivatives graphene oxide (GO) and reduced GO (rGO) show outstanding structural, electrical, optical, catalytic and mechanical properties and are thus increasingly used in many applications, which could lead to their release into the environment. Further, graphene NMs can adsorb organic pollutants, hence they could act as carriers of these pollutants to organisms.

In this work, we investigated the bioavailability and adverse effects of water-borne metal-bearing NPs (Ag, Au, CdS, CuO, SiO_2, TiO_2 and ZnO) in mussels *Mytilus galloprovincialis* and zebrafish *Danio rerio*, as sentinel and model aquatic organisms, in comparison to bulk and ionic forms of the same metals. For this, both *in vitro* and *in vivo* approaches were applied. *In vitro* cell-based assays and embryo toxicity tests provide quick and reproducible high throughput tools for the screening of NP toxicity and mechanisms of action. *In vivo* experiments allow assessing adverse effects using a battery of molecular, cellular and tissue-level biomarkers. Results allowed to classify studied NPs based on their toxicity to mussel cells *in vitro* and to zebrafish embryos. Overall, NP forms were less toxic than ionic forms but more toxic than the bulk forms, suggesting that observed responses were partly due to dissolved metals. NP toxicity depended on their physico-chemical properties and their behaviour in exposure media (aggregation, dissolution). Ag, CdS and CuO NPs were the most toxic NPs tested and SiO_2 NPs the least toxic. Size, mode of synthesis and the presence of additives influenced NPs toxicity. Common mechanisms of action of Ag, CdS and CuO NPs were ROS production and oxidative stress, DNA damage and activation of lysosomal activity and MXR transport activity in mussel cells. Effects on hemocyte phagocytic activity were particle specific on exposure to CdS and Ag NPs. In zebrafish, Ag, CdS and CuO NPs were internalized and caused an array of sublethal effects from changes in liver transcriptome to gill histopathologies. In a separate set of experiments of dietary exposure to 5 nm Ag NPs, food web transfer of Ag NPs was demonstrated, from the microalgae *Isochrysis galbana* to mussels and from the crustacean *Artemia* brine shrimp to zebrafish, with subsequent deletereous effects on exposed organisms and also on their offspring (embryo malformations). Finally, a similar *in vitro* and *in vivo* approach is being adopted to assess the internalization and toxicity of graphene derivatives. GO, GO-PVP and rGO-PVP showed low and dose-dependent cytotoxicity to mussel hemocytes, increased ROS production and caused a significant decrease in plasma membrane (PM) integrity. Graphene nanoplatelets were internalized by disrupting hemocytes´s PM and by endocytic mechanisms. In exposures of hemocytes to graphene with adsorbed oil compounds, these increased nanoplatelets toxicity indicating that graphene nanoplatelets may act as “Trojan horse” carriers of oil compounds. Overall, obtained data may contribute to the risk assessment of nanomaterials in the environment and to the development of safe-by-design approaches to produce safer environmentally sustainable nanomaterials.

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Chemically propelled motors: an introspection into their operational mechanisms

Maria Jose Esplandiu
Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain
Mariajose.esplandiu@icn2.cat

One of the main challenges in the engineering of micro/nanomachines is the quest for efficient mechanisms to power them without using external driving forces. Under this context nature is a source of inspiration. The engineering of self-propelled micro/nanomachines with the capability to emulate biological motors has become a research line of growing interest since the pioneering studies at the beginning of this millennium. These micro/nanomachines generate and harness local physicochemical gradients to drive their own motion and at the same time, they can perform multitasking activities. Although the proofs of concept for applications have been significant, the progress on the comprehension of the physicochemical fundamentals behind the self-generated actuation has been more moderate. In many cases, the precise motion mechanism is still not unambiguously identified, and the key physicochemical parameters are not well-characterized. A complete and deep understanding of such issues would help to improve the control levels for applications and to better assess perspectives and challenges of these self-propelled machines.

In this presentation, we will focus on chemically driven motors whose motion is the result of a complex interplay of chemical reactions and (electro)hydrodynamic phenomena. A reliable study of these processes is rather difficult with mobile objects like swimming motors. Therefore we have resorted to pumps, which are the immobilized motor counterparts. Thus pumps emerge as simple manufacturing and well-defined platforms for a better experimental probing of the mechanisms and key parameters controlling the actuation.

We will review a combined set of techniques that we have implemented to study chemically propelled micropumps[1,2,3]. These techniques have turned out to be very useful for mapping chemical reactions and for extracting physicochemical parameters (e.g. electric fields, fluid flows) and thus to achieve a more complete characterization of the mechanisms driving fluid motion. We will mainly focus on metallic/semiconductor motors to analyze light-controlled motion mechanisms through photoelectrochemical decomposition of fuels. In these systems, we found a very interesting competition between two different mechanisms for fluid propulsion stemming from different chemical pathways in the fuel decomposition. The studies with pumps are very relevant for their swimmer counterparts, shedding light on their motion mechanisms and providing useful clues for the design and optimization of phoretic systems.

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Structural Design and Biotecnological Applications of Nanoporous Anodic Alumina

Josep Ferré-Borrull, Laura Pol, Chris Eckstein, Laura K. Acosta, Elisabet Xifre-Pérez, Lluis F. Marsal

Universitat Rovira i Virgili, Nano-electronics and Photonic Systems Group (NePhoS)
Avinguda Paisos Catalans 26, Tarragona, Spain
josep.ferre@urv.cat

Nanoporous Anodic Alumina (NAA) is a material with great versatility and low-cost and scalable production. In the last years, the group NePhoS led by Prof. Lluis F. Marsal has reached a high level of expertise on the preparation of such material and its application to health, energy and environment., as it has been reported in previous communications to Nanospain. In this communication we aim at introducing the latest advances in structural design of NAA and its application to the biotechnological domain. Structural desing refers to providing different function to the basic porous oxide material through changes in the structure during production and engineering of its optical properties.

One of the applications of NAA is the development of a nano-opto-fluidic method to detect changes on the geometry or the surface properties of the pores in NAA[1,2], which permits the detection of the binding of different proteins to the pore walls. The second example shows that the precise control of the fabrication parameters permits the achievement of rugate filters with photonic stop bands that can be applied to biosensing [3,4]. Finally, we show the ability of NAA to monitor in real time the attachment of different biomolecules to the pore walls by means of an optical spectroscopy method and adequate post-processing.

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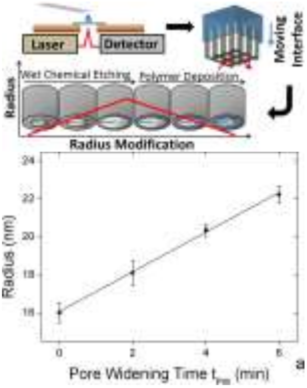

Figure 1: Fluid Imbibition-coupled interferometry (FICLI).

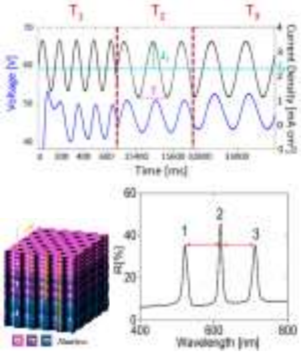

Figure 2: Stacked rugate filters with tunable high reflectance stop bands.

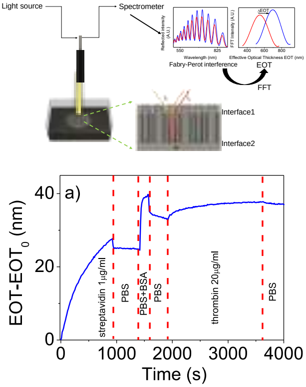

Figure 3: Reflection Interference Spectroscopy (RIfS) for real time monitoring of molecule interaction.

C. elegans a powerful screening biotool for nanotechnology

A. Laromaine, L. González- Moragas, Z. Luo, A.Muñoz-Juan, S. Y. Srinivasan
Nanoparticles and Nanocomposites Group(www.icmab.es/nn) Institut Ciencia de Materials de Barcelona (ICMAB-CSIC)
Campus UAB, 08193 Bellaterra, Spain alaromaine@icmab.es

Nanoparticles (NPs) offer the possibility to chemically and structurally tune their properties impacting on how they interact with biological materials. Hundreds of NPs have been proposed as drug carriers and therapies, however the lack of a time- and batch-efficient method to evaluate NPs and processes prevents establishing general fundamental principles and impedes the progress of these future drugs and therapies unless high throughput methods advance.

Biopolymers, probiotics and dietary fibers are also currently in exploration to fight metabolic diseases such as diabetes, linked to obesity. However, those polymers are frequently tested based on trial and error on humans.

In this context, *Caenorhabditis elegans* (*C. elegans*) emerges as an ideal biotool to evaluate nanomaterials. *C. elegans* is an invertebrate, transparent worm with high genetic homology to humans. The gastrointestinal tract (GI) of this worm shares traits to the humans; we use the GI as test-bed for the multiparametric optimization of those nanomaterials, in specific in applications by oral delivery. The use of this *in vivo* metrology reduce the number of higher animals used, complying with the 3R principles, and speed the process of translation of drugs and food complements to the market.

The combination of anatomical, biochemical and genetic tools with materials science characterization techniques in the tiny *C. elegans in vivo* and at multiple biological levels (whole organism, organs, tissues, cells and pathways) will breakthrough in the engineering of food components for oral delivery decreasing time and cost effort.

In this presentation, we will show how *C. elegans* is becoming a powerful biotool to evaluate nanoparticles ranging from oxides to metal nanoparticles or polymers.

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Atomically-precise graphene nanoarchitectures

C. Moreno, M. Vilas-Varela,[1] B. Kretz,[2] A. Garcia-Lekue,[2,3] M. V. Costache, M. Paradinas, M. Panighel, M. Tenorio, G. Ceballos, S. O. Valenzuela,[4] D. Peña,[1] and A. Mugarza[4]

Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain.
[1]Centro de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela. Santiago de Compostela 15782, Spain.
[2]Donostia International Physics Center, Paseo M. de Lardizabal 4, 20018 San Sebastian, Spain.
[3]Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain
[4]ICREA Institució Catalana de Recerca i Estudis Avançats, Lluis Companys 23, 08010 Barcelona, Spain
(corresponding author: C. Moreno, e-mail: cesar.moreno@icn2.cat)

Nanosize pores can turn semimetallic graphene into a semiconductor and from being impermeable into the most efficient molecular sieve membrane. However, scaling the pores down to the nanometer, while fulfilling the tight structural constraints imposed by applications, represents an enormous challenge for present top-down strategies.

Here we report a bottom-up method to synthesize nanoporous graphene comprising an ordered array of pores separated by ribbons, which can be tuned down to the one nanometer range (1-3). The size, density, morphology and chemical composition of the pores are defined with atomic precision by the design of the molecular precursors. Our DFT-STS study further reveal a highly anisotropic electronic structure, where orthogonal one-dimensional electronic bands with an energy gap of ~1 eV coexist with confined pore states that can be regarded as 2D analogues of the superatom states found in fullerene. The combined structural and electrical properties makes this nanoporous 2D material a highly versatile semiconductor for simultaneous sieving and electrical sensing of molecular species.

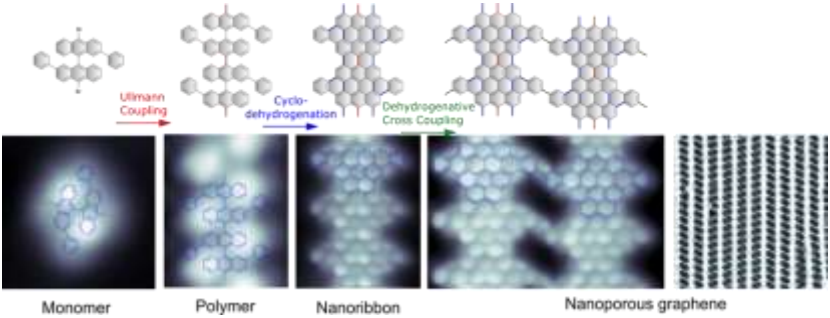

Figure1. *STM images (bottom) and schematic representation (top) of the precursor, intermediates and final product of the hierarchical synthesis of nanoporous graphene.*

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From FIB to advanced FIB Nanofabrication: Taking advantage of multiple Ion Species and large Area Nanopatterning

F. Nouvertne, S. Bauerdick, A. Nadzeyka, P. Mazarov and L. Bruchhaus

Raith GmbH Dortmund, Konrad-Adenauer-Allee 8, 44263 Dortmund, Germany
frank.nouvertne@raith.de

Multi-technique nanofabrication instrumentation comprising both an electron and an ion beam optics (FIB-SEM systems) have proven to be flexible multi-purpose tools enabling 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 fully unlock their true nanopatterning potential and to secure stable, reproducible, highest precise and efficient operation for optimum results and device performance - also over large areas - advanced hardware, patterning control and strategies for these tools come into play.

That has been accomplished with our latest generation of FIB (and SEM-) technology integrated into a true lithography platform optimized for nanometer scale patterning over large areas and extended periods of time. 2D-and 3D-applications in quantum technologies, optics, telecommunication, plasmonics, nanofluidics and nanobiotechnology, such as X-ray zone plates [1], large area gratings [2], plasmonic arrays, and wafer-scale nanopore devices have successfully been demonstrated. Innovative stitching error free patterning modes enabled by a high precise laserinterferometer controlled stage provide access to nm-scale patterning in the cm-regime.

Since the type of used ion species has dramatic consequences on the nature of the interaction mechanism with the sample and thus the resulting nanostructures, we have extended the ion column towards the long-term stable delivery of multiple species for a nanometer-scale focused ion beam employing a liquid metal alloy ion source (LMAIS). The column is equipped with a mass filter capable of selecting from various ion species [3]. This provides single and multiple charged species of different mass without changing the source. We present the capabilities of the multiple-species FIB instrument for sub-20 nm nanofabrication employing ions like Si and Au.

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Figures

Figure 1: True 3D in one go: micro-fluidic mixer by simultaneously controlling both lateral shape and depth of the structure, fabricated with FIB.

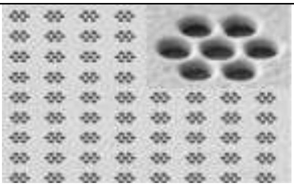

Figure 2: Plasmonic structure with sub 30nm rims between the circles, nanofabricated by FIB with extremely low intensity beam tails

Bio-hybrid nanorobotic devices: towards healthcare applications.

Tania Patiño,[1,2] Ana Hortelao,[2] Xavier Arqué,[2] Samuel Sánchez.[2, 3]

University of Rome Tor Vergata, Department of Chemistry, University of Rome, Tor Vergata, Via della Ricerca Scientifica 1, Rome 00133, Italy
Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology, Baldiri Reixac 10-12, Barcelona 08028, Spain
Institució Catalana de Recerca i Estudis Avançats (ICREA), Pg. Lluís Companys 23, Barcelona 08010, Spain

tpatino@ibecbarcelona.eu

Bio-hybrid nanorobotic devices are able to self-propel thanks to the enzymatic conversion of substrates into products.[1] Their unique properties, including biocompatibility, fuel bioavailability and active motion could revolutionize current drug delivery approaches based on passive micro- and nanodevices. In fact, we have recently demonstrated that enzyme-powered nanobots are able to increase drug release efficiency in a fuel-dependent manner.[2] In addition, we have observed that targeting capabilities are also improved with active motion when using nanomotors functionalized with an Anti- Fibroblast Growth Factor Receptor III (FGFR3) against 3D bladder cancer spheroids.[3] We further engineered enzyme-powered micromotors through DNA nanotechnology in order to make them able to sense the pH of their surrounding environment using pH responsive DNA nanoswitches.[4]

Despite the exciting advances in the field, a deeper fundamental knowledge is required in order to continue developing micro- and nanomachines able to move and perform tasks in different contexts.[5] In this regard, we investigated the effect of enzyme quantity and distribution on the motion dynamics of urease-powered micromotors through stochastically optical reconstruction microscopy (STORM).[6] Lastly, intrinsic enzyme properties and their effect on active motion where also studied by a combination experimental and Molecular Dynamics simulations approach.

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Self-assembly methods for nanoelectronics

Francesc Perez-Murano, Laura Evangelio, Steven Gottlieb, Marta Fernández-Regúlez,
Christian Pinto-Gómez, Esteve Amat, Alberto del Moral, Joan Bausells

Institute of Microelectronics of Barcelona (IMB-CNM, CSIC). Campus UAB, 08193 Bellaterra, Spain

For many decades, miniaturization has been the driven force for the evolution of the microelectronics industry. In recent years, advances in high-resolution lithographic and nano-fabrication techniques have raised the possibility to obtain nanoelectronic devices approaching the single nanometre scale. Size scales of ~20 nm or even less can now be achieved using advanced optical lithography in combination with multiple patterning, as well as by alternative lithography methods such as scanning probe lithography, state-of-the art high-resolution electron beam lithography, and material modification techniques such as focused ion-beam patterning [1]. However, it is still missing a lithography method that combines single nanometer resolution along with high throughput, low defectivity and affordable costs. These three last conditions are necessary for the industrial future relevance of nanoelectronic devices.

A complementary approach to pure top-down lithography based fabrication is the use of self-assembly methods, in which small entities define the smallest parts of the devices. In this talk, we will present two approaches in which we have been involved during the last years: directed self-assembly of block copolymers [2,3] and self-assembly of nanocrystal in nanopillars [4]. In the first case (Figure 1), we have developed methods to create guiding patterns that orientate thin films of block copolymers. In the second case, ion exposure of nanowires and nanopillars create embedded silicon crystals, which can be used to generate a single electron device.

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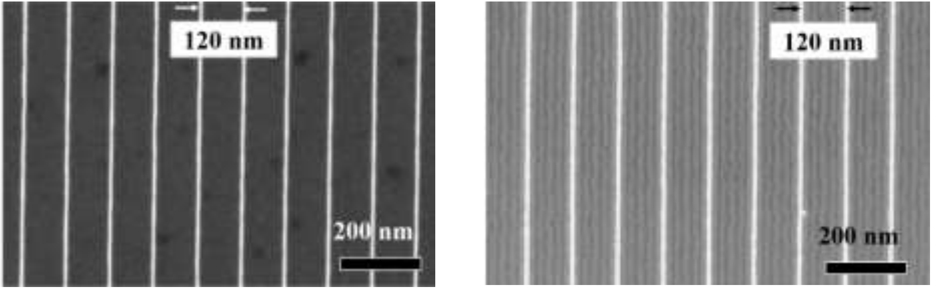

Figure 1: Example of directed self-assembly of block copolymers. The image on the left shows a guiding pattern composed of silicon oxide lines of 9 nm width. The image on the right shows the result of the self-assembly of PS-b-PMMA block copolymers directed by this guiding pattern. [3]

Chromium Halides: Recent Progess and Open Questions

David Soriano, Claudia Cardoso and Joaquín Fernández Rossier

Radboud University, Institute for Molecules and Materials, NL-6525 AJ, Nijmegen, the Netherlands
d.soriano@science.ru.nl

The discovery of 2D ferromagnetic insulators[1,2] have strongly boosted the design and engineer of new van der Waals devices through the combination of different layered materials with different electronic properties[3-5]. Although the magnetic properties of these materials have been already reported experimentally using optical[2] and transport probes[6], a miscroscopic magnetic theory for these materials is still lacking and correlation effects are far from being completely understood.

In this talk, I will show some recent progress in understanding magnetism in chromium halides from first-principles calculations. More specifically, I will describe stacking-dependent magnetism in bilayer CrI3[7] and how proximity effects in CrI3/Graphene interface may play an important role in the stacking properties of few layer CrI3.

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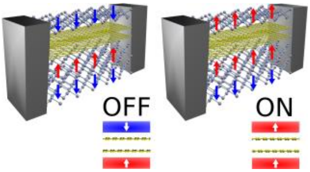

Figure 1: Spin-valve device based on CrI3/Graphene van der Waals heterostructure.

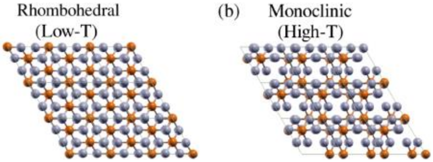

Figure 2: Low vs. High temperature stacking of bilayer CrI3.

Graphene for detection and creation of terahertz light

Klaas-Jan Tielrooij[1], Sebastián Castilla[2], Bernat Terrés[2], Marta Autore[3], Rainer Hillenbrand[3], Frank Koppens[2], Hassan Hafez[4], Sergey Kovalev[5], Michael Gensch[5], Dmitry Turchinovich[4]

[1]Catalan Institute of Nanoscience and Nanotechnology (ICN2), Barcelona Institute of Science and Technology (BIST), Bellaterra (Barcelona), Spain
[2]ICFO – The Institute of Photonic Sciences, Barcelona Insitute of Science and Technology (BIST), Castelldefels (Barcelona), Spain
[3]CIC NanGUNE, Donostia-San Sebastian, Spain
[4]Bielefeld University, Bielefeld, Germany
[5]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
klaas.tielrooij@icn2.cat

The interaction between low-energy photons in the terahertz (THz) spectral range and graphene gives rise to a number of interesting physical phenomena that will likely become technologically relevant. As a first example, I will show our recent results on using graphene for detecting THz light [1]. We have demonstrated that the dominant mechanism that gives rise to a THz-induced photoresponse is the photo-thermoelectric effect: absorbed THz light leads to carrier heating in graphene, and if this happens at a *pn*-junction with an asymmetry in the Seebeck coefficients, this gives rise to an electrical photoresponse. We have developed a simple analytical model to describe this effect, and have used this to design and fabricate a novel, antenna-integrated, graphene THz photodetector. The detector (see Figure 1) exhibits excellent sensitivity (noise-quivalent power <100 $pW/Hz^{1/2}$), and a very short switching time (<30 ns, setup-limited). Furthermore, it operates at room temperature and for a range of THz frequencies that is only limited by the antenna. These specifications make the device already commercially competitive. As a second example, I will mention the recent demonstration of highly efficiently generated THz harmonics (up to 7th order) in graphene, which is enabled by THz-induced carrier heating-cooling dynamics in graphene and its back-action on incident THz radiation [2].

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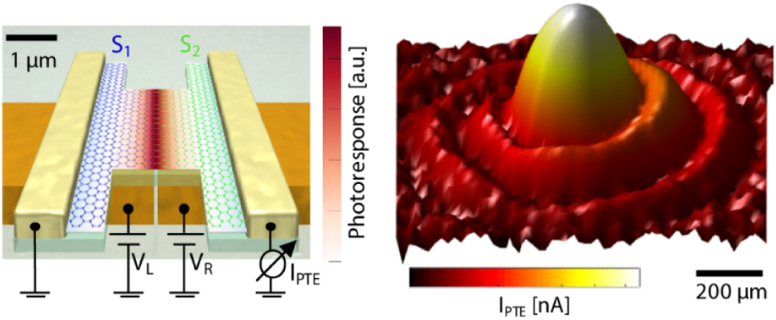

Figure 1: (Left) Schematic layout of the main part of the THz photodetector, showing an H-shaped graphene channel on top of the central part of the antenna, with the antenna gap. Voltages V_L (V_R) are applied to the left (right) antenna branch, thus creating the *pn*-junction with asymmetric Seebeck coefficients (S_1 and S_2), leading to a photo-thermoelectric photocurrent I_{PTE}. (Right) Measured photocurrent, scanning the device through a THz focal plane. The observation of multiple fringes of the Airy pattern illustrates the high sensitivity of the device.

Oral contributions

DFT study of the electrical and thermal transport properties of 2D MoS_2: Application to thermoelectricity

Dr. Christophe A. Adessi, S. Pecorario, S Thébaud and G. Bouzerar
Institut Lumière Matière, UMR 5306 Université Cluade Bernard Lyon 1 – CNRS, Université de Lyon, 69622 Villeurbanne CEDEX, FRANCE
christophe.adessi@univ-lyon1.fr

Transition metal dichalogenides like MoS_2 have received an increased interest as a new family of two dimensional (2D) materials. Unlike graphene, MoS_2 exhibit a large band gap and have already been used promisingly as field effect transistor[1]. Moreover, 2D materials are expected to lead to higher thermoelectric figure of merit compared to bulk materials due to poor thermal conductivity[2]. However, we have pointed out in a previous work, that doping is a delicate task with MoS_2 in order to obtain good electrical properties[3]. The challenge associated with thermolectricity is to minimize thermal transport and maximize electrical transport as the thermoelectric figure of merit ZT is defined as:

$$ZT=\frac{\sigma . S^2}{\kappa} . T$$

where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity and T the temperature. During this talk, I will address the influence of a very common kind of defects in MoS_2 which are the sulfur vacancies. I will present the influence of this defects on both the electrical and the thermal transport properties of MoS_2. For this work, DFT calculations have been used, combined with the Landauer formalism allowing us to investigate more realistically the influence of the disordering of the sulfur vacancies. One of the main result is the very different behavior of the ZT depending if the material is n or p doped.

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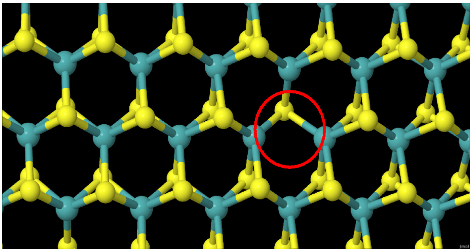

Figure 1: MoS_2 with a single sulfur vacancy.

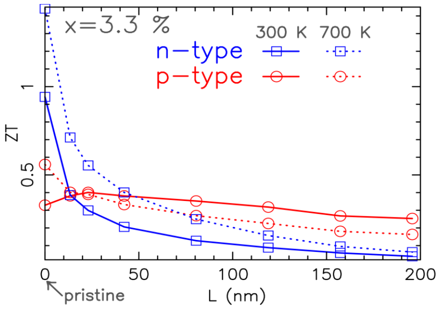

Figure 2: Figure of merit ZT for MoS_{2-x} as function of the length of the system either doped with electrons or holes for 2 temperatures.

An-all atom investigation on morphological stability and transport properties of Reduced Graphene Oxide

Aleandro Antidormi[1], Luciano Colombo[2], Stephan Roche[1]

[1] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193, Barcelona, Spain
[2] Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, I-09042 Monserrato (Ca), Italy
aleandro.antidormi@icn2

Reduced Graphene Oxide (RGO) is a material resulting from the (chemical or thermal) reduction of Graphene Oxide. There is general consensus that RGO can be described as a random distribution of oxidized areas bearing the oxygenated functional groups, separated by nonoxidized regions wherein most of the carbon atoms preserve sp^2 hybridization [1]. Despite numerous spectroscopic studies, poor information on the density and types of defects generated during the reduction process together with their spatial distribution is yet available.

Hence, a detailed study of the atomistic structure of RGO represents a crucial step toward understanding the properties of this material and its effect on thermal and electronic properties.

In this study, we use molecular dynamics simulations to mimick the process of high-temperature thermal reduction of an oxidized graphene sheet by simulating the structural evolution of defects and impurities. Starting from several sheets differing for oxidation level and impurity composition, we examine the concentration of carbon atoms sp-2 hybridized, and hence the integrity of the resulting material.

Moreover, the effect of the annealing temperature and of the spatial distibution of functionalizing agents (epoxy and hydroxyl groups) on the overall sample morphology is also investigated.

The corresponding thermal and electron conductivities are then calculated, highlighting the strong dependence of on the application performance on the fabrication parameters.

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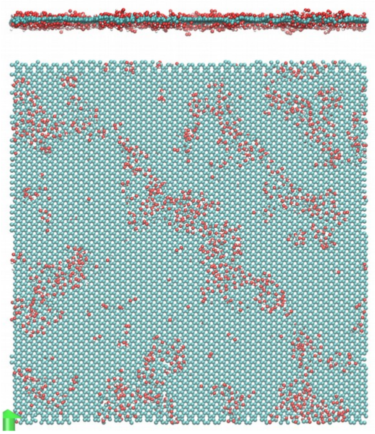

Figure 1: Side and top view of a GO sample before thermal reduction.

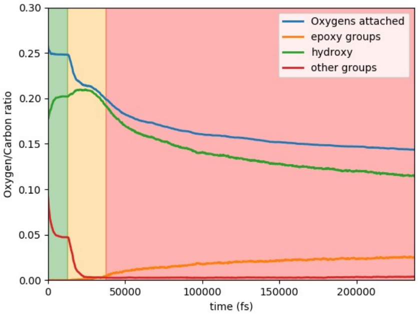

Figure 2: Evolution of the functionalizing groups on a GO sample during thermal annealing (T=1000K).

Toxicological profile of bioaerosols in industrial and urban scenarios – case studies in the framework of worker risk assessment

Arantxa Ballesteros-Riaza[1], Nuria Ruiz-Costa[2], Maidá Domat-Rodríguez[1], Oscar Andreu-Sánchez[2]
[1] ITENE Research Center, C/Albert Einstein 1 - 46980 Paterna, Valencia (Spain) arantxa.ballesteros@itene.com
[2] Xenobiotics S.L., C/Catedrático Agustín Escardino 9 - 46980 Paterna, Valencia (Spain)

Exposure assessment to nanomaterials (NMs) in industrial workplaces shows that the handling of manufactured NMs may give rise to occupational exposure to primary NPs (which have their origin in the emission resulting from industrial activities, or due to background aerosols), but also urban environments are susceptible to present them.

Emerging and Newly Identified Health Risks[1] found that there were proven health hazards associated with a number of manufactured nanomaterials. Not all nanomaterials necessarily have a toxic effect, however, and a case-by-case approach is necessary while ongoing research continues, and the concern about them has been subject of numerous studies.[2] [3] The health impacts deriving from inhalation of NPs results from their capacity to penetrate into the deeper sections of the respiratory tract due to their small size has been established.[4]

The present work aims to assess the toxicolocial profile of bioaresols sampled on both industrial and environmental places, focusing in the evalution off occupational exposure to engineered nanoparticles under real-world operating conditions in the plastic sectot. Apart from the toxicological study, the approach also contemplated the characterization fo NPs exposure (physical, morphological, chemical) and the characterization of the handled nanomaterial (dustiness), in order to be able to make a better interpretation of the dat resulting

Therefore, framing the worker exposure study in a risk assessment approach, the toxicological profile of samples collected in workplaces were assessed. Considering inhalation as the most common route of exposure, cytotoxic assays were developed under the adenocarcinomic human alveolar basal epithelial cell line A549 through the MTT Proliferation Assay. Samples in bioaerosol form were collected in cell culture medium by a BioSampler®.

The trend in the results in toxicity assays showed moderate cytotoxic effect of the bioaerosols, with an average cell viability of 65%. By not discriminating by nanoparticle, the study of bioaerosols does not lead to the conclusion that there is a potential effect for the specific nanomaterials studied here or not, but it is very important to have an idea of the effect that the work environment can have for workers. Proper air quality monitoring to detect the presence of NPs in the environment can be a good starting point for the proper risk assessment and management associated with NMs.

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Figures

Figure 1: (BioSampler adapted to the BioLite+ Pump sampling bioaerosol during working operations in a graphene-based materials company).

HoF_3 and DyF_3 nanoparticles as dual contrast agents for MRI and CT

A. I. Becerro,[a] D. González-Mancebo,[a] A. Corral,[b] M. Balcerzyk,[b]
M.L. García-Martín,[c] J.M. de la Fuente,[d] M. Ocaña[a]

[a]Instituto de Ciencia de Materiales de Sevilla (CSIC-US-JA) Spain; [b]Centro Nacional de Aceleradores (CSIC-US-JA) Spain
[c]BIONAND (JA-Universidad de Málaga and CIBER-BBN) Málaga, Spain; [d]Instituto de Ciencia de Materiales de Aragón (CSIC-University of Zaragoza, and CIBER-BBN) Spain. Contact@E-mail: anieto@icmse.csic.es

Use of contrast agents (CAs) is frequently necessary in MRI (Magnetic Resonance Imaging) to increase the contrast between normal and abnormal tissues. Clinically used MRI CAs are based on gadolinium chelates and superparamagnetic iron oxide nanoparticles (SPIONS). Recently, Gd-based inorganic nanoparticles, such as $NaGdF_4$,[1] appeared as an interesting alternative due to their excellent contrast enhancement, long circulation times and the possibility of target specificity, which leads to reduced dose and minimized damage to normal tissues. However, although Gd-based nanoparticles provide good contrast characteristics at low magnetic fields, they are less effective at high magnetic fields, and this is also the case of Gd-chelates and SPIONS. MRI scanners working at high magnetic fields (>7 T) are more and more demanded nowadays as they increase sensitivity and shorten acquisition times.[2] Therefore, new CAs need to be developed to improve diagnostic capabilities of the new generation of high field MRI scanners. Dy^{3+} and Ho^{3+} are two ions that are suitable for high field T_2 CAs due to their large magnetic moment without saturation of the magnetization at very high magnetic fields.[3] The purpose of this work is to synthesize uniform, water dispersible LnF_3 (Ln= Ho, Dy) nanoparticles, using homogeneous precipitation in polyol medium, and to evaluate their relaxivity at high magnetic field (9.4 T), to be used as MRI CAs in biomedicine. In addition, due to their high atomic number, these DyF_3 and HoF_3 nanoparticles show high X-ray attenuation capacity, which confer a double functionality to the probes, both as MRI and X-ray Computed Tomography CAs.

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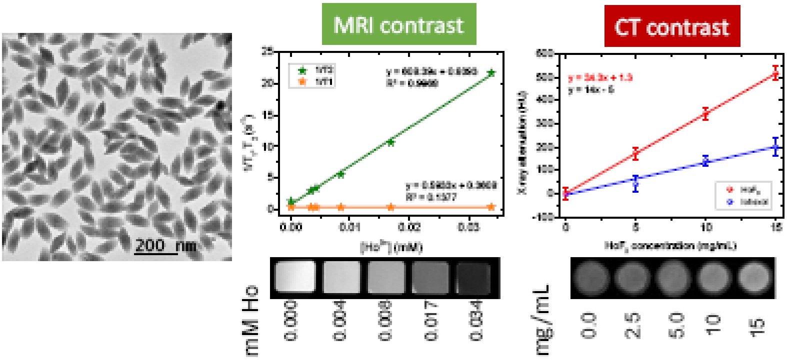

Figure 1: Left: TEM micrograph of HoF_3 nanoparticles synthesized in ethylene glycol at 120ºC. Middle: T1 and T2 proton relaxivity plots and phantoms obtained at room temperature using a 9.4 T magnet in aqueous suspensions of HoF_3 nanoparticles. Right: X-ray attenuation values of HoF_3 nanoparticles in aqueous suspensions and their phantom images.

Exploring Atomic Layers for Photocatalysis

Ravi K. Biroju[1*], Rahul Sharma[2], Alexander J. Pattison[1], Balakrishna Ananthoju[3], Robert A.W. Dryfe[3],
Tharangattu N. Narayanan[2] and Wolfgang Theis[1]

[1]Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham B15 2TT, UK
[2]Tata Institute of Fundamental Research, Sy. No. 36/P, Gopan Pally Village, Serilingampaly Mandal, Ranga Reddy District, Hyderabad- 500 107. Telangana, India
[3]School of Chemistry, National Graphene Institute, University of Manchester, Manchester M139PL, UK
*Contact@R.K.Biroju@bham.ac.uk

Abstract

Two-dimensional (2D) layered materials exhibit exceptional properties, such as high carrier mobility, wide range of light absorption/emission and relatively narrower band gap, which make them ideal candidates for the construction of novel photocatalysts[1]. 2D layered semiconductors, such as semiconducting transition metal dichalcogenides (STMDs) are the new members of 2D materials family that consist of a “sandwich” structure of a transition metal layer (e.g. M: Mo, W) covalently bonded between two chalcogen layers (e.g. X: S, Se, Te) to form MX2: MoS_2, WS_2 etc. They have gained worldwide attention in recent years. Engineering various combinations of STMDs based on stacking sequence, alloying and crystal phase will provide unique opportunities to tailor new -dedicated materials for different applications.[2-3] Vertical/lateral vdW STMDs heterostructures have attracted considerable research interest due to their efficient electron-hole separation during the conversion of light to current, and these have found use in high- performance optoelectronic devices and photocatalysts. In this talk, I demonstrate the fabrication and characterization of MoS_2 and WS_2 based atomic layers and their alloyed versions withof ‘Se’ ($MoS_{2(1-x)}Se_{2x}$, $WS_{2(1-x)}Se_{2x}$). Morphology and crystalline quality of alloys are assessed using Raman and X-ray photoelectron spectroscopy. In particular, homogeneity of layers (mono and few layers) and alloying of Se over mono and few layer MoS_2 and WS_2 are estimated from HAADF-STEM imaging. In addition, I will present density functional theory calculations in order to estimate the charge density distribution between S and Se on the MoS_2 basal plane, which shows S in the Se environment has higher charge density compared to S without Se which makes it active towards hydrogen evolution reaction (HER) activity.

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Figures

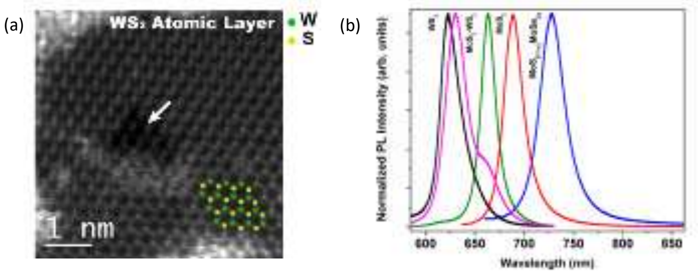

Figure 1: (a) Atomic resolution HAADF STEM image of single layer WS2 and an arrow indicates a S vacancy. (b) Tunable photoluminescence from MoS_2, WS_2 based vdW STMDs

Nature-Inspired nanocomposites enabling smart technologies

José Manuel Delgado-López, Gloria B. Ramírez-Rodríguez

Bionanomet, department of Inorganic Chemistry, University of Granada, Spain.
jmdl@ugr.es

Bone has a hierarchic structure with many levels of organization [1]. Different supra-fibrillar arrangements occur and coexist, forming dense structural hierarchies from the nanoscopic to the macroscopic length scales [1]. The building block of such a complex architecture at the atomic-namometer length scales is the mineralized collagen fibril. Over the past years, new insights into the mechanisms of bone mineralization have been reported; however, open debates still persist concerning the chemical nature of the first mineral formed; the factors controlling the initial deposition and growth of crystals; the role of the organic matrix (*i.e.* collagen, non-collageneous proteins (NCPs) and small molecules) [2]. Numerous studies were focused on exploring the role of collagen and NCPs suggesting that they may be involved in different steps of bone mineralization, such as the formation of the precursor phase(s), its further transformation into and organization of apatite crystals [2]. However, most of the above-mentioned questions still remain unanswered or at least under discussion [3].

We are interested in understanding how higher organisms produce their specialized mineralized structures, with special emphasis on elucidating the mechanisms (i.e., nucleation and crystal growth) enabling the control over the final crystal size, morphology and polymorphism. We are also keen in turning the gained knowledge into the design of novel materials with higher level of performance and new functionalities: i) collagen/mineral hybrid nanocomposites for hard tissue repair;[4] ii) CaPs nanocarriers of targeting moieties, therapeutic and imaging agents;[5] iii) fluoride-doped CaP nanoparticles for enamel remineralization.[6] Some of the latest results will be presented.

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Mesoporous Silica Nanocontainers: State of Art and Outlooks

O.V. Dement'eva[1], K. A. Naumova[1,2], S.K. Zhigletsova[3], Yu.I. Kuznetsov[1], V.M. Rudoy[1]

[1]Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, 119071, Leninsky prospect 31, Moscow, Russia
[2] Moscow State University, 119992, Vorob'evy gori 1, Russia
[3]State Research Center for Applied Microbiology & Biotechnology, 142279, Obolensk, Russia
dema_ol@mail.ru

The problems of encapsulation of various functional substances (first of all, water-insoluble or slightly soluble ones), as well as their controlled release, are of great importance for biomedicine, pharmaceutics, material protection, etc.

Here we discuss the prospects for solving these problems using mesoporous silica nanocontainers (MSNs) prepared by the sol–gel method. We are focused on the new concept of encapsulation of amphiphilic functional compounds which have been developed by us earlier. It is based on the using of associates (micelles or vesicles) of these substances (instead of similar associates of "inert" surfactants) as templates in MSNs synthesis. This allows us to combine the stages of the MSNs synthesis and their loading with such functional substances and to provide their very high content in the particles. The benefits of this approach are demonstrated using a wide range of amphiphilic compounds, including antiseptics, an anticancer drug and corrosion inhibitors.

The effects of the template structure and sol–gel conditions on the morphology and loading capacity of MSNs are analyzed quantitatively.

The main features of the templating functional substance's release from the MSNs into the aqueous environment are studied, and a mechanism of this process is proposed. It is shown that the templating substance release is determined by the solubility and/or swelling of the silica matrix under the action of penetrating water and the interaction of its molecules/ions with the pore walls of the MSNs. The rates of these processes are strongly dependent on the medium pH.

The bactericidal activity of encapsulated antiseptics against the *Staphylococcus aureus* is evaluated *in vitro* by agar diffusion method.

The possibility of sol–gel synthesis of multifunctional MSNs using the "hybrid" templates, which are presented by the micelles of antiseptics containing solubilized hydrophobic drug, has been demonstrated.

It is revealed that the MSNs which have been prepared using the corrosion inhibitor micelles as templates can be easily incorporated into the paint and varnish coatings (in contrast to "pristine" inhibitor). Such coatings provide a very effective protection of low-carbon steel and D16 aluminum alloy against corrosion even under severe conditions of neutral salt spray.

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Continuous phase transition of the MoS_2 from 2H to 1T' state by using 2D electride: Ca_2N

Krishna P Dhakal,[1]*Ganesh Ghimire,[1,2] Kyungwha Chung,[1] Yeji Kim,[1,2] Sung Wng Kim,*[1,2] Jeongyong Kim*[1,2]
[1]Department of Energy Science, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea. [2]Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Suwon 16419, Republic of Korea
Email address: dhakal@skku.edu, kimsungwng@skku.edu, j.kim@skku.edu

Abstract

The lattice engineering of the sulfide based transition metal dichalcogenide (TMDs) is difficult compared to selenide and telluride materials.[1] Here, we report on the continuous phase transition of the few layers to bulk molybdenum disulfide (MoS_2) system by realizing the hetero-structures with the low work function (2.6 eV) two dimensional electride (2D-$[Ca_2N]^+\cdot e^-$) that contain highly mobile electrons[2], where the large work function differences (>2 eV) between them is the key of the degenerate electrons doping that is distributed over a distance of few tens of nanometer from the contact interface in contrast to the other surface limited (~1 nm) chemical functionalizations or ionic gating approaches.[3] An electron doping density of ~10^{14} cm^{-2} was estimated on the MoS_2 layers that performed exceptional layer thickness dependent lattice symmetry change from the 2H to 1T′ phases until a few-layer (~10 nm) and then strong doping effect to the bulk samples resulting a giant band gap re-normalization by ~200 meV along with the softening of the commonly observed Raman modes by the $\Delta\omega$=10 cm^{-1}. As the MoS_2 thickness was decreased, well defined Raman peaks of 2H crystal were gradually disappearing along with the emergence of other 1T' phase Raman modes, thus elucidating the symmetry change feature due to concentrated charge density in a thinner film. Additionally, a hetero-structure of the few-layer MoS_2 demonstrated multiple in-plane anisotropic Raman modes, including those of metallic phases Raman modes along with the presence of the hugely shrunk (250 meV) optical gap and enhanced PL intensity than a pristine monolayer MoS_2; a realization of the few-layer 2H-MoS_2 crystal with distorted symmetry and direct band gap structure when placed on the top of the $[Ca_2N]^+\cdot e^-$. This is attributed to the long-range electron doping induced structural change across the K-Γ line, hence provided an opportunity to discover various kinds of 2D materials using a single 2D-dopant suitable for the future optoelectronic application.

KEYWORDS: MoS_2, electride, doping, long range, phase-transition, direct band gap structure

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Role of cerium in activating solar fuels production in transition metal-oxides

I. Di Bernardo, X. Gao, P. Kreider, W. Lipinski and A. Tricoli

The Australian National University, ACT Campus, Canberra, Australia
iolanda.dibernardo@anu.edu.au

Earth abundant and environmentally friendly transition metal oxides are attracting broad research for thermochemical redox cycles. Despite progress, a major challenge is ensuring fast and reversible redox kinetics and large oxygen exchange capacities.

We provide insights on the role of Ce dopants in unlocking the redox capacity of manganese oxide nanoparticles, via the formation of an intermediate carbide stage [1, 2]. We perform a detailed analysis of the structural evolution and chemical composition of the material during the redox steps, as a function of the cerium content, by combining synchrotron-based spectroscopy (NEXAFS, in-depth XPS profiling) and in-house microscopy (SEM, TEM). We observe that in every cycle the cerium atoms migrate from the bulk to the surface of the 20nm-nanoparticles and back, and that the presence of cerium in 3+ oxidation state both within the lattice of the metal oxide and on its surface is essential to the formation of the carbide phase, ensuring high and stable reduction kinetics. This is optimally achieved for a cerium content of 3%. Smaller Ce content (1%) are insufficient to stabilize the redox reactions resulting in the rapid growth of the manganese oxide grains, while higher doping content (5%) cause the rapid segregation and inactivation of Ce.

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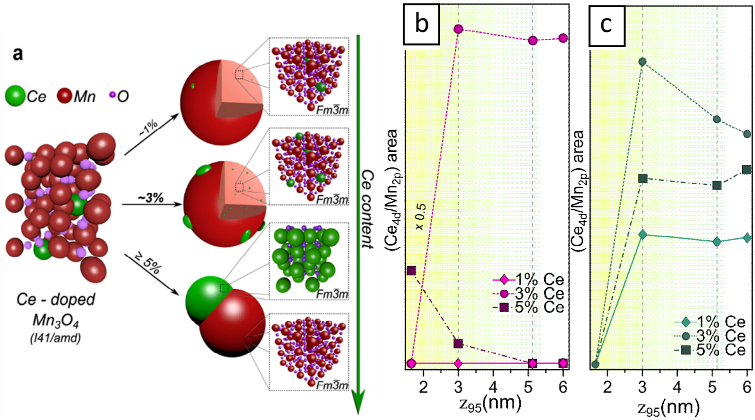

Figure 1: a) Proposed simplified schematics of the structural enhancement mechanism of the optimally doped Ce compounds as a function of the Ce content. b, c) Ce concentration in the MnO nanoparticles, in the reduced and oxidized stage respectively, as a function of the distance from the surface (z95) for different initial Ce doping concentration.

Solution-processed organic lasers with top-layer nanostructured resonators

María A. Díaz-García[1,2], Víctor Bonal[1,2], Rafael Muñoz-Mármol[1,2], Marta Morales-Vidal[1,2],
José M. Villalvilla[1,2], Pedro G. Boj[1,3], José A. Quintana[1,3]

Dpto. Física Aplicada[1], Inst. Universitario de Materiales[2] and Dpto. Óptica[3], Universidad de Alicante, Alicante 03080, Spain
maria.diaz@ua.es

Solution-processed organic lasers are very attractive light sources due to their advantages of chemical versatility, wavelength tunability, mechanical flexibility and low cost. Particularly interesting for applications in the fields of optical communications, biosensing and chemical sensing are distributed feedback (DFB) lasers, consisting of nanostructured active organic waveguides. In this presentation we will discuss recent advances of our research group towards improving both, the active laser material and the laser resonator. Particularly, we will focus on lasers with a novel device architecture (Figure 1) with a resonator fabricated by a method developed in our laboratory, consisting on a top-layer polymeric layer with an holographycally engraved one-dimensional relief grating, which shows various advantages with respect to other configurations [1]. We will show results for different types of active laser materials, including organic compounds, such as as carbon-bridged phenylenevinylene oligomers [2] or polymers [3], perylenediimide dyes [4] and other very novel nanomaterials related to graphene.

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Figures

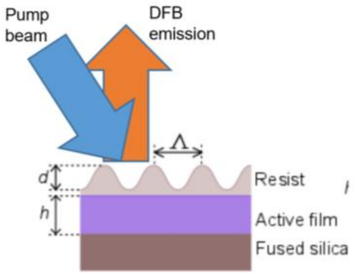

Figure 1: Sketch of organic DFB laser with top-layer polymeric resonator, including pump and collection geometry.

Synthesis of Solid and Hollow Metal/CeO_2 Hybrid Nanostructures

Neus G. Bastús[1], Jordi Piella[1], Javier Patarroyo[1], Florind Merkoçi[1], Aziz Genç[1],
Jordi Arbiol[1, 2] and Victor Puntes[1, 2,3]

[1] Institut Català de Nanociència i Nanotecnologia (ICN2), CSIC, The Barcelona Institute of Science and Technology (BIST), Campus UAB, Bellaterra, Barcelona, Spain.
[2] Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain.
[3] Vall d'Hebron Institut de Recerca (VHIR), 08035, Barcelona, Spain.
neus.bastus@icn2.cat

Controllable integration of noble metals and metal oxides into single nanostructures has recently become one of the hottest research topics due to the unique structural features and synergetic optical and catalytic properties that these complex nanocrystals (NCs) possess. In quest of developing advanced functional NCs, the design of metal-oxide nanostructures has become quite sophisticated through controlling the size, shape and crystal structure of the constituent domains. Still, a long-standing barrier has been the development of simple and cost-effective synthetic processes allowing a fine adjustment of the structure and interface of these systems. Until now, a great deal of work has been performed to design and produce different nanostructures containing noble metal (Pt, Pd, Au, Ag) cores and CeO2 shells with outstanding optical and catalytic properties. However, the synthetic protocols for the production of these NCs have become considerably more and more complicated as the control of NC's morphology and architecture becomes more precise, often requiring multiple steps and exotic techniques.

Herein, we present a general approach for the preparation colloidal solutions of metal/CeO2 hybrid NCs that allow the fine adjustment of the final composition, location engineering (core/shell or heterodimer), dimensionality and surface structure of each individual domain.[1] As a result, we obtain Au/CeO2 and Ag/CeO2 hybrid NCs with precise control of their size and morphology. Moreover, by using these NCs as a template and adopting the galvanic replacement reaction to oxidize the Ag counterpart, hollow hybrid structures AgAu/CeO2, AgPt/CeO2, and AgPd/CeO2 can be prepared. The combination of noble metal and CeO2 domains in a well-defined architecture represents the possibility to tune the optical and catalytic activity and selectivity of the resultant NCs.

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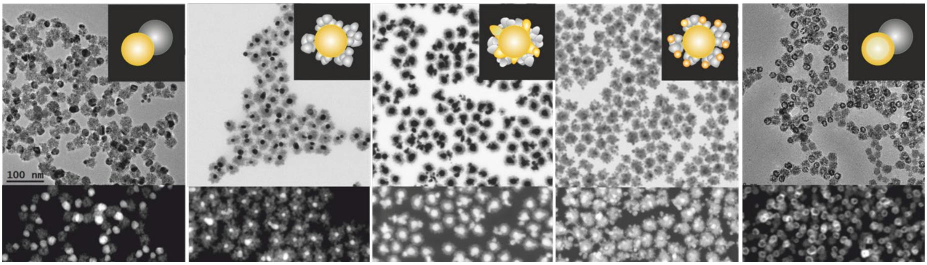

Figure 1: *Representative examples of the hybrid solid and hollow metal/CeO2 NCs produced with controlled size, shape, morphology and architecture.*

Facile synthesis of NHC-stabilized Ni nanoparticles and their catalytic application in selective hydrogenations

Aitor Gual,[a] Miriam Díaz de los Bernardos,[a] Sara Pérez-Rodríguez,[a] Carmen Claver,[a,b] and Cyril Godard[b]
[a] Centre Tecnològic de la Química (CTQC) - EURECAT, 43007 Tarragona, Spain
[b] Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, 43007 Tarragona, Spain
aitor.gual@ctqc.org

Metal nanoparticles (M-NPs) combine advantages of both homogeneous and heterogeneous catalysts, namely high activity /selectivity and facility for recycling and re-use. To enhance their catalytic performance, it is necessary to induce control on the physical and chemical properties of the M-NPs. Previously, we have demonstrated that strongly-coordinating ligands are able to efficiently induce this control.[1] Here, we present a new and facile procedure to synthesize metal NPs stabilized by strongly coordinating N-heterocyclic carbene (NHC) ligands. To date, similar NHC-stabilized NPs were prepared by complicated multi-step synthesis and required the use of strong bases. Our approach is one pot procedure involving in-situ generation of free NHC-ligands through decarboxylation of 1,2-dimethylimidazolium-2-carboxylate (Me_2Im-CO2) under M-NPs preparation reaction conditions. This new methodology has been successfully applied preparation of colloidal and immobilized Ni-NPs.[2] The catalytic performance of these materials on selective hydrogenations has been evaluated.

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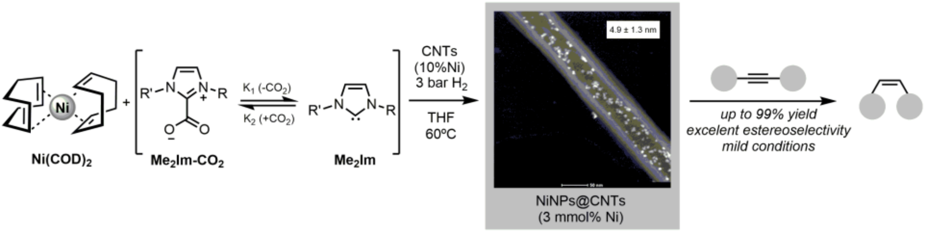

Figure 1: Synthesis NHC-stabilized metal nanoparticles and catalytic application in selective hydrogenation.

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Multifunctional nanostructured composite aerogels from a molecular-free gelation process

Pablo Guardia, Taisiia Berestok and Adnreu Cabot

1) Catalonia Institute for Energy Research – IREC, 08930 Sant Adrià de Besòs, Barcelona, Spain,
2) ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain
pguardia@irec.cat

Inorganic nanocrystals (INCs) have been already exploited as building blocks to produce nanostructured gels and aerogels. However, the poor mechanical stability of the gels, the use of advance surface functionalization for gelation and the limitations to perform multicomponent gels are still unaddressed issues. Graphene based gels partially overcome those limitations showing outstanding mechanical and chemical stability, but still gelation processes require for molecular ligands at mild conditions and gels' functionalities are rather limited. Here, we report on a molecular-free gelation process to synthesize reduced GO-INCs (rGO-INCs) nanostructured composite aerogels. Different to what has been so far reported, INCs (e.g. Fe_2O_3, CeO_2, In_2S_3, ZnS and Au) are directly exploited as the gelation agent to produce rGO-INCs aerogel composites while adding functionalities to the graphene porous structure. Through a suitable functionalization of INCs, hydrogels are formed by mixing them together with GO nanosheets in an aqueous solution at mild conditions. After drying under supercritical CO_2 conditions, aerogels with high surface area and functional properties (magnetic, photo catalytic, etc) are produced. The final high porous nanostructured composite consists of a rGO structure, that act as an scaffold providing stiffens and electric conductivity, interconnected through INCs that act as the binding agent. Our approach is rather flexible and robust providing large aerogels (in this particular work aerogels havin volumes up to 10 mL) with multiple functionalities. The latter are achieved by mixing more than one type of INCs together with GO nanosheets. As a result, binary, ternary and quaternary multifunctional aerogels showing magnetic, plasmonic, luminescent and photocatalytic properties can be produced. This approach opens a newway to produce multifunctional porous platforms with high mechanical properties and tailored functionalities for sensing, water purification or energy storage applications.

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Figures

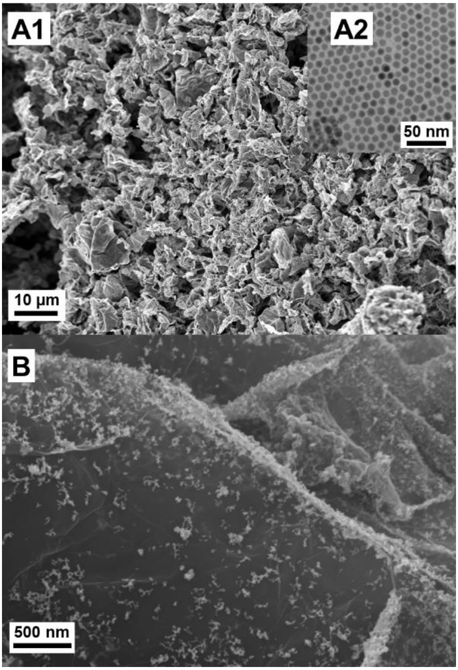

Figure 1: Structural characterization of graphene based (GO-Fe2O3) nanocomposite aerogels.

The Preparation of Nanoparticles Based on Unsaturated Fatty Acid Impregnated Chitosan Membrane for Using in Cancer Related Infections

Ebru Kilicay[2], Abdullah Kizaloglu [1] , Zeynep Karahaliloglu[3], Baki Hazer[4,5], Emir Baki Denkbas[6,7]

[1] Bülent Ecevit University, Institute of Science, Nanotechnology Engineering Department, 67100, Zonguldak, Turkey
[2] Bülent Ecevit University, Zonguldak Vocational High School, Kilimli, 67500, Zonguldak, Turkey
[3]Aksaray University, Faculty of Science, Biology Department, 68000, Aksaray, Turkey
[4]Department of Aircraft Airflame Engine Maintenance, Kapadokya University, Mustafapasa Kasabası, Universite Meydanı, 50420, Ürgüp, Turkey

[5]Department of Chemistry, Bulent Ecevit University, Universite Caddes, 67100, Zonguldak, Turkey

[5]Department of Nano Technology Engineering, Bulent Ecevit University, Üniversite Caddesi, 67100, Zonguldak, Turkey

[6]Hacettepe University, Institute of Pure and Applied Scinces, Bioengineering Division
06800 Beytepe, Ankara, Turkey

[7]Başkent University, Faculty of Engineering, Department of Biomedical Engineering, 06530 Bağlıca, Ankara, Turkey
ebru.kilicay@gmail.com

The present study includes the design of a chitosan membrane decorated with unsaturated fatty acid based carrier system for cancer treatment and antibacterial application. For this purpose, a suitable drug with antitumoral and antimicrobial properties was loaded into nanoparticular formulation and the nanoparticle formulation was embedded into chitosan membrane in order to prevent tumor-associated infections that may occur due to the weakening of the immune system during the cancer treatment. In this study, poly styrene-graft-poly oleic acid-g-poly ethylene glycol graft copolymers (PS-g-Poleic-g-PEG) were prepared by free radical polymerization and the physicochemical characterization was carried out via Fourier-transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (H-NMR). Pristine PS-Poleic-PEG nanoparticles and the different concentrations [2:1-1:1 polymer/drug (w/w)] of caffeic acid loaded PS-Poleic-PEG NPs were prepared by solvent evaporation technique.The size-size distribution of NPs was performed by changing the some parameters. The short term stability of NPs were investigated at 4 °C in storage conditions for 30 days. Drug encapsulation and loading efficiency of drug loaded NPs were also evaluated. The chitosan membrane and the chitosan membrane with Caff NPs were sucessfully fabricated. The chitosan-caff-NPs composite membrane showed controlled release during about 50 days. The mechanical properties of obtained chitosan membrane-drug loaded nanoparticles and chitosan membrane were observed higher than for chitosan membrane-naked nanoparticles. The Caffeic acid NPs-composite membranes indicated excellent antibacterial properties than the chitosan membrane against the Escherichia coli and Staphylococcus aureus. In vitro culture medium of SaOS-2 human osteosarcoma and MC3T3-E1 osteoblast cell lines, the anticancer activity of the all samples was evaluated by MTT assay and verified through the flow cytometry and double staining methods. As a results, the designed novel drug delivery platform showed great potential to cancer-associated infections treatment in bone cancer cases

Quatsomes: a novel, thermodynamically stable nanovesicle system

Mariana Köber[1], Lidia Ferrer-Tasies[1,2], 1, Sílvia Illa-Tuset[1], Dganit Danino[3], Jan Skov Pedersen[4],
Jaume Veciana[1,2], Jordi Faraudo[1], and Nora Ventosa[1,2]

1 Institut de Ciència de Materials de Barcelona (CSIC), and 2 Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Campus Universitari de Bellaterra, E-08193 Cerdanyola, Spain; 3 Department of Biotechnology and Food Engineering, Technion - Israel Institute of Technology, Haifa 32000, Israel; 4 Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, 8000 Aarhus, Denmark
ventosa@icmab.es

Thermodynamically stable nanovesicles form a distinguished and particularly interesting class of vesicles, especially for pharmaceutical applications that require a long shelf-life and outstanding vesicle integrity during blood circulation. Due to the poor long-term stability of liposomes, there is a large interest in identifying alternative, non-phospholipid building-blocks, which self-assemble into stable vesicles and satisfy the quality standards for pharmaceutical formulations. We have developed a new nanovesicle system based on the self-assembly of quaternary ammonium surfactants and sterols in aqueous phases.[1] These non-liposomal bilayer vesicles, which we have termed quatsomes, show diameters of about 40 nm, exhibit positive charged surfaces, and can be precisely decorated with multiple targeting groups.

Here we present experimental as well as theoretical evidence that quatsomes form a thermodynamic equilibrium system. Next to the outstanding stability of these nanovesicular architectures and the high homogeneity in vesicle size, lamellarity and composition,[2] we will discuss some further quatsome characteristics that substantiate their high potential for applications in nanomedicine, such as a low toxicity and the possibiltity to be used as protein nanocarriers[3,4] as well as for bioimaging[5,6].

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Mapping the ionic conductivity of a solid polymer electrolyte by non-contact AFM

Daniel E. Martínez-Tong[1,2], Paul Markus[3], Georg Papastavrou[3], Angel Alegria[1,2]

[1]Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU). P. Manuel de Lardizabal 3, E-20018 San Sebastiań – España
[2]Centro de Física de Materiales (CSIC – EHU/UPV). P. Manuel Lardizabal 5, Donostia 20018 – España.
[3]Department of Physical Chemistry II. Faculty of Biology, Chemistry & Earth Sciences. Universität Bayreuth – Alemania.

danielenrique.martinezt@ehu.eus

The study of the physical properties at the nanometer scale is becoming a key aspect for understanding the relations between the molecular organization and physical behavior in nanostructured polymers. For example, AFM-based electrical measurements in polymers are increasingly used to map the nanoscale conductivity in systems with potential applications, as semiconductors and electrolytes. Typically, this requires setting-up an electrical contact with the polymer surface, usually done by bringing the AFM probe into direct contact with the sample. However, since polymers are soft materials, these contact-based techniques might lead to sample scratching and plastic deformation. To overcome this issue, in this work we present "nanoDielectric Spectroscopy (nDS)". [1,2] This non-contact AFM technique allows the electrical mapping of surfaces, by applying an AC bias to the AFM probe at a fixed electric field frequency (f). nDS provides maps with information related to the components of the complex dielectric permittivity (ε^*) of the samples. In addition, it is possible to carry out dielectric spectroscopy measurements (f = 1 Hz – 100 kHz) at fixed points on the sample's surface (Figure 1). These measurements can be analyzed under the framework of classical electrodynamics and allow the study of transport properties. As a case of study, we will present nDS experiments on poly(ethylene oxide) (PEO) thin films. PEO is a semicrystalline polymer that at room temperature shows a dielectric relaxation signal related to charge trapping between amorphous/crystalline interfaces. This phenomenon is connected to the ionic conductivity of the amorphous phase of the material. We will present nDS images and spectra of PEO at room temperature, with 40 nm lateral resolution, and in a humidity range of 15 – 60%. The nDS results were analyzed taking into consideration the role of the tip/sample geometry and allowed us to obtain the material's complex dielectric function. We modeled our results following the Maxwell-Wagner-Sillars theory. This provided relevant physical parameters such as the DC-conductivity of the amorphous phase, and its dependence with relative humidity.

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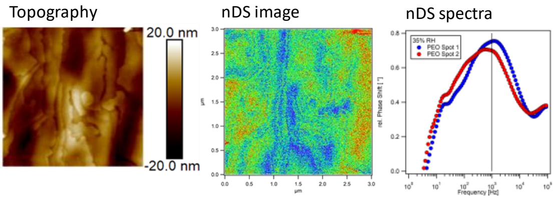
Figures



Topography

nDS image

nDS spectra

Figure 1: AFM topography image of a PEO film (left) and nanoDielectric Spectroscopy measurement (right).

AuAg hollow nanoshells as therapeutic tools for cancer treatment

Mondragón L[1-3], Russo L[1-3], Patarroyo J[1-3], Merkoci F[1,2], Piella J[1-3], Bastús N[1-3] and Puntes V[1-5]

[1]CSIC, Catalan Inst Nanosci & Nanotechnol ICN2, Campus UAB, Barcelona 08193, Spain; [2]BIST, Campus UAB, Barcelona 08193, Spain; [3]Univ Autonoma Barcelona, Campus UAB, E-08193 Barcelona, Spain; [4]Vall dHebron Inst Recerca, Barcelona 08035, Spain; [5]ICREA, P Lluis Co 23, Barcelona 08010, Spain – e-mail: victor.puntes@icn2.cat

It has become widely accepted that none of the existing single-modality treatments (immunotherapy, chemotherapy, radiotherapy, gene therapy or thermotherapy) can cure fatal diseases such as cancer by itself. Consequently, different combinations of these treatments have been tested for their synergistic effects that may dramatically improve outcomes by reducing the side effects of each single modality treatment. This is because therapeutic effects add up while side effects are distributed[1]. Au nanoparticles (AuNPs) provide a broad range of biomedical applications thanks to their possible use in a number of techniques for cancer imaging, diagnosis and treatment[2]. All these applications rely on on the so-called localized surface plasmon resonance phenomenon (LSPR), taking place when an AuNP is irradiated with an electromagnetic wave. Then, its conduction electrons will be driven by the electric field to collectively oscillate relative to the lattice of positive ions, creating intense peaks (both scattering and absorption) at resonant wavelenthgs.

However, prior the development of these multimodal NPs there are important question that need to be address being the integration of the NPs and their properties in the standard models of ADME (Administration, Distribution, Metabolization/Transformation/Degradation and Excretion). For that purpose, we describe the synthesis of monodisperse AuAg hollow nanoshells which is obtained by means of a highly reproducible and robust methodology based on the galvanic replacement reaction[3,4]. This is possible thanks to the systematic identification of the role played by the different synthetic parameters involved in the process (such as surfactants, co-oxidizers, complexing agents, time, and temperature), providing an unique control over the morphological and optical properties of the material[4]. At the same time, we have developed an in vivo biodistribution study in order to determine: where the NPs go, how they evolve and how they end-up while delivering drugs and serving as antennas for real time monitorization, and validate the extend of their capabilities on therasnotic future applications.

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Superperiodicity Induced Band Gap In Graphene

M. N. Nair, I. Palacio, A. Celis, A. Zobelli, A. Gloter, S. Kubsky,
J-P. Turmaud, M. Conrad, C. Berger, W. A. de Heer, E. H. Conrad
A. Taleb-Ibrahimi, and A. Tejeda

KU Leuven, Oude Market 13, 3000 Leuven, Belgium
Contact@maya.nair@kuleuven.be

Although graphene hosts a number of fascinating properties suitable for nanoelectronic applications, it lacks a sizeable energy gap in its electronic structure. Numerous methods have been proposed to produce a semiconducting graphene [1,2]. We have recently shown a band gap of more than 0.5eV in buffer layer graphene, i.e. the precursor growth state of graphene [3].

By using different experimental techniques such as scanning tunneling microscope (STM), high-resolution scanning transmission electron microscope (HR-STEM) and angle-resolved photoemission spectroscopy (ARPES), we show that the band structure in the buffer has an electronic periodicity related to the structural periodicity observed in STM and X-ray diffraction [4]. Our ARPES analysis confirmed the observed bandgap is due to the super periodicity induced by the substrate [5].

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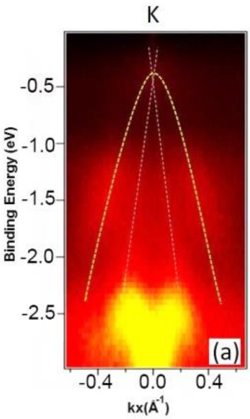

Figure 1: ARPES band structure of buffer layer graphene

Laser fabrication of nanocarbon-based hybrid electrodes for supercapacitors

Ángel Pérez del Pino[1*], Enikö György[1,2], Pablo García Lebière[1], Fernando Pantoja-Suarez[3,4], Roger Amade[3,4], Enric Bertran-Serra[3,4]

1 Instituto de Ciencia de Materiales de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain
2 National Institute for Lasers, Plasma and Radiation Physics, P. O. Box MG 36, 77125 Bucharest, Romania.
aperez@icmab.es
3 ENPHOCAMAT Group, Department of Applied Physics, Universitat de Barcelona, Martí i Franquès 1,
E-08028 Barcelona, Spain
4 Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona, Spain

Low dimensional carbon materials, particularly graphene derivatives and carbon nanotubes (CNT), in combination with transition metal oxide (TMO) nanostructures are being intensively investigated for energy storage applications due to their outstanding physical and chemical properties [1,2]. The synthesis of this type of materials through conventional methods can reveal drawbacks as chemical incompatibilities, solubility limitations or problems for producing additional compounds in contact with thermally sensitive materials. Alternatively, localized extreme heating produced by pulsed laser radiation appears as a valuable tool for rapid, non-toxic and versatile synthesis of these compounds [3,4].

The aim of this presentation is to show results concerning the development of CNT-TMO and reduced graphene oxide-TMO-based hybrid materials obtained through direct laser irradiation as well as matrix assisted pulsed laser evaporation (MAPLE) techniques. Structural characterization and thermal simulations reveal that the laser irradiated materials (CNT, graphene oxide, TMO nanoprecursors) undergo ultrafast heating mechanisms, reaching very high temperatures in confined regions. These extreme conditions promote the activation of extensive thermochemical processes in addition to selective recrystallization of the nanostructures, leading to the synthesis of a rich diversity of nanomaterials. The effects of the laser radiation on the structural as well as supercapacitive energy storage properties of the irradiated / deposited electrode materials will be discussed.

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Figures

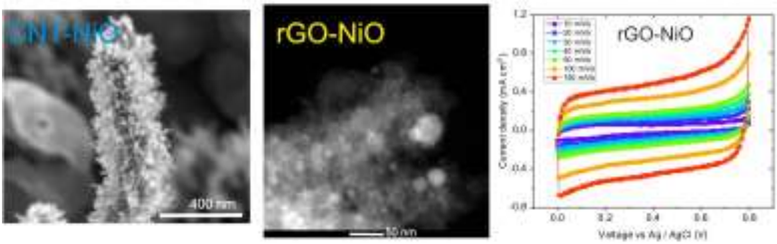

Figure 1: SEM image of CNT-NiO and STEM image of reduced graphene oxide (rGO)-NiO materials, as well as cyclic voltammetries of rGO-NiO electrode.

The Kernel Polynomial Method in Kwant, Open-Source Software for Nanoscale Simulations

Pablo Piskunow[1], Joseph Weston[2], and Anton Akhmerov[3]

[1]Catalan Institute of Nanoscience and Nanotechnology, UAB Campus, Barcelona, 08193, Spain
[2]QuTech, Delft University of Technology, Lorentzweg 1, 2628CJ Delft, The Netherlands
[3]Kavli Insittute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628CJ Delft, The Netherlands
pablo.perez.piskunow@gmail.com

Nanoscale simulations in condensed-matter, and realistic nanoscale devices are generally limited in size by computational requirements. Here, we present the kernel polynomial method (KPM) that has a linear scaling with the system size [1], which allows efficient calculations of physical properties over large systems. The KPM module is embedded into Kwant [2], an open-source software package, which offers an accessible entry point for quantum simulations.

The most basic application of the KPM module is to obtain the density of states of a closed system. Furthermore, with the KPM, the spectral density of any operator can also be obtained in linear time.

Later on, we will show the usage of the KPM in obtaining the Kubo conductivity. The implementation is based on the Kubo-Bastin formula [3], that allows the simulation of the conductivity tensor for non-zero temperatures. The KPM expansion of the conductivity tensor can be generalized to calculating the correlation matrix between any two operators. This greatly expands the field of possible applications to other observables, such as the optical conductivity.

Finally, we will show an example of using the KPM to calculate topological invariants [5], by expanding the projector on the ground state, and evaluating a local real-space expression of the Chern number for two-dimensional systems, and the winding number for one-dimensional and three-dimensional systems.

These examples show the versatility of the KPM module, that together with the linear scaling of spectral densities, makes it a very efficient tool for simulating devices at the nanoscale.

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Ultra-long, continuous and super-flexible glass nanofibers produced by a novel technique: Continuous Fiberizing by Laser melting and Supersonic dragging.

F. Quintero[1], J. Penide[1], AJ Palomares-García2, JM. Molina-Aldareguia[2], A. Riveiro[1], J. del Val[1], R. Comesaña[3], F. Lusquiños[1], J. Pou[1]

1. Applied Physics Department, Universidade de Vigo, EEI, c/ Maxwell s/n, 36310 Vigo, Spain.
2. IMDEA Materials Institute, c/Eric Kandel 2, 28906 Getafe, Madrid, Spain.
3. Department of Materials Engineering, Applied Mechanics and Construction, University of Vigo, EEI, c/ Maxwell s/n, 36310 Vigo, Spain.

fquintero@uvigo.es

The necessity of materials with improved mechanical properties has driven the production of high performance fibers. The development of nanofibers and nanotubes predicted the production of new nano-composites with exceptional mechanical properties. However, the breakthrough predictions haven't been achieved jet, in part due to the reduced length of the nanofibers or nanotubes, which restrained the mechanical reinforcement and manufacturing. Consequently, there is an enormous interest in the development of advanced continuous nanofibers, but conventional methods for fiber spinning cannot produce fibers thinner than some micrometers robustly.

Here we present a novel and unique method to produce extremely flexible glass nanofibers, with diameters that range from 300 nm up to 30 µm and virtually unlimited length. The process essentially consists on heating the precursor material uniformly and extremely fast using a high power laser beam while, at the same time, the melt is rapidly stretched and cooled by the supersonic air jet. The temperature distribution must be precisely controlled by selecting the laser beam parameters in order to obtain the proper viscosity to guarantee filament stability. With this aim, an specifically conceived laser beam shaping system was designed and set-up. Concurrently, a supersonic gas flow is ejected using a de Laval nozzle expressly designed to provide an uniform supersonic air jet flowing coaxially with the filament, so that it exerts a high tension localized along the molten segment of the filament, which is essential for the rapid stretching and cooling of the nanofiber. A suitable combination of these tools permits rapid heating, stretching and cooling of the precursor material, which is a key factor to produce fibers with small diameters, preventing filament rupture or devitrification in continuous and stable process.

This new method allows producing extremely long continuous nanofibers, virtually infinite, giving total control of diameter, and, since it is a bushing-free technique, it can be employed to process compositions with high fiber forming temperatures. In the present work we demonstrate the production of pure silica continuous nanofibers, analyze their structure and, remarkably we present a preliminar assessment of their mechanical properties using a set of innovative techniques. The results reveal a tensile strength of our glass nanofibers in the same order as high performance fibers, but having a notable flexibility attaining radius of curvature of 10 µm.

Biomimetic calcium phosphate nanoparticles as promising nanocarriers for sustainable agriculture

Gloria B. Ramírez-Rodríguez,[a,b] Eva Pérez-Álvarez,[c] Cristina de Miguel Rojas,[d] Francisco J. Carmona-Fernández,[b] Gregorio dal Sasso,[e] Alejandro Pérez-de-Luque,[d] Teresa Garde-Cerdán,[c] Antonietta Guagliardi,[e] Norberto Masciocchi[b] and José Manuel Delgado-López[a]

[a] University of Granada, department of Inorganic Chemistry, Faculty of Science, Av. Fuente Nueva, s/n, Granada, Spain. [b] University of Insubria and Total Scattering Laboratory, Via Valleggio 11, Como, Italy. [c] IFAPA Alameda del Obispo, Area of Genomic and Biotechnology, Córdoba, Spain. [d] Institute of Grapevine and Wine Sciences-CSIC, Logroño, Spain. [e] Institute of Crystallography (CNR) and Total Scattering Laboratory. Via Valleggio 11, Como, Italy.
gloria@ugr.es

The application of conventional fertilizers, supplying the macronutrients as nitrogen (N), phosphorus (P) and potassium (K), is one of the current solutions to face the increase in global food demand.[1] However, only a small percentage of the NPK nutriens is assimilated by the plants, being the rest eventually washed into water bodies through leaching and surface run-off, or lost by volatilization under reduced conditions. Indeed, the low nutrient use efficiency (NUE) of convential treatments is causing serious environmental consequences, such as eutrophication.[1] Thus, the use of more efficient practices is crucial for ensuring increasing yields without compromising environmental integrity or public health.[1] Nanotechnology offers great promises as an innovative tool for a controlled and efficient delivering of active species in plants.[2] Biomimetic calcium phosphate (CaP) nanoparticles, similar to the mineral component of bone and teeth, have been widely explored in nanomedicine as bone-repair materials and multifunctional nanocarriers.[3] In fact, CaPs exhibit excellent biocompatibility and biodegradability, can be easily doped or functionalized with active species (e.g., plant macronutrients) and show a pH-dependent solubility and thus, a pH-responsive release of the loaded species.[4] Despite all these exceptional properties and the fact that they are intrinsically rich in P and Ca (important plant macronutrients), very few reports can be found about the use of CaP nanoparticles in Agriculture.[5,6] Nonetheless, the doping of CaP nanoparticles with essential macronutrients has not been yet explored. We will show a simple and easily scable protocol to obtain multinutrient nano-fertilizers based on the doping of calcium phosphate (CaP) nanoparticles. The nano-fertilizers have been in-depth characterized in terms of composition, structure and particle size. We have demonstrated that the nanoparticles in aqueous media provide a slow and gradual release of the macro- and micronutrients. Experiments on plants have been also performed to demonstrate the increase of NUE with the use of nanoparticles in comparison with conventional treatments. This work opens the possibility to engineer complex nanofertilizer (NPK) with multiple nutrient kinetic for targeted treatment in agriculture.

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Nanoscale approach in mineralogy and its implications in ore deposits.

Josep Roqué-Rosell[1,2], Abigail Jiménez-Franco[1,2,3*], Thomas Hans Aiglsperger[4], Joaquín A. Proenza[1,2],
Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Marti i Franquès s/n, Barcelona, Catalunya 08028, Spain.
2. Institut de Nanociència i Nanotecnologia, IN2UB Facultat de Química, Universitat de Barcelona
Av. Diagonal 645, 08028 Barcelona, Catalunya, Espanya
3. Posgrado en Ciencias de la Tierra, Universidad Nacional Autónoma de México, Ciudad Universitaria, Delegación Coyoacán, 04510 Cd. de México, México.
[4]Luleå University of Technology, Department of Civil Engineering and Natural Resources, Division of Geosciences and Environmental Engineering, SE 97187 Luleå, Sweden.

Although nanoscale studies in minerals science have increased in the last decade, the number of publications in this field continue being scarce. By contrast, FIB/SEM/TEM techniques are now well established [1], especially for analysis of silicate minerals (e.g. [2]). Regard to ore minerals, recent studies have taken relevance, especially to explain the behavior of minor and trace elements in different geochemical systems [3, 4]. The submicron structural study of the natural occurring ore minerals can be used to resolve several questions about their origin by understanding their forming conditions, growth and structure.

In the present work, FIB/SEM/TEM coupled with EDS and PED showed its great potential for studying the structure of heterogeneous mineral that are otherwise difficult to study by conventional methods because of their small crystal size, low purity, and high structural complexity. We also want to remark that the followed approach to identify and characterize the crystal structure on otherwise ‘‘too-small-to-study” minerals or aggregates can be directly applied to any type of naturally occurring as polycrystalline aggregates that are of interest in earth sciences, environmental sciences and related disciplines.

By combining the chemical composition (obtained from the EDS mapping) and the crystalline structure identification (obtained from PED-based crystal phase maps) at sub-micron scale, for the first time we can study the crystallographic structure of small gold nuggets in lateritic soils (Figure, 1). This is an example of an emerging field of research in earth related sciences and shows how advanced electron microscopy, if focused on sites of metallogenetic interest, can provide new insights into ore deposit formation.

Figure 1: Gold crystal orientation maps obtained by means of PED (a) zone axis identification distribution yellow (4 1 9) blue (8 7 9) and pink (-3 -2 -9), (b) the goodness of fit map in grayscale showing the darkest areas that correspond to the grain boundaries with unassigned zone axis, (c) composite image with zone axis identification and goodness of fit and (d) zone axis and the corresponding color scale.

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Nanofunctionalised materials based on polyoxometalate-polymer interaction

Leire Ruiz-Rubio[1,3]**,** Beñat Artetxe[2], Leyre Pérez-Álvarez[1,3], Juan Manuel Gutierrez-Zorrilla[2,3], José Luis Vilas-Vilela[1,3]

1Macromolecular Chemistry Group (LABQUIMAC), Department of Physical Chemistry, University of the Basque Country (UPV/EHU
2 Department of Inorganic Chemistry, University of the Basque Country (UPV/EHU)
3 BCMaterials, Basque Center for Materials, Applications and Nanostructures Organization, Address, City, Country
Leire.ruiz@ehu.eus

The versatility and diversity of application areas of organic-inorganic hybrids have improved the interest of the researchers, as exemplified by polymeric systems that incorporate polyoxometalate (POM) anions. POMs are anionic clusters formed by the combination of oxygen and early transition metals V, Mo or W in their highest oxidation states that can exhibit a wide variety of properties, sizes and structures as well as potential applications in fields like catalysis, materials science and biomedicine.

Methods: In this work, we have developed two different POM-based polymeric hybrid material (Figure 1). On the one hand, considering the anticancer properties of some POMs, chitosan-based nanocarries have been synthetized by microemulsion and loaded with bioactive $[P_2Mo_{18}O_{62}]^{6-}$ anions. The physicochemical properties of this system have been thoroughly characterized, in addition to their application as drug delivery system. On other hand, another interesting property of POMs is their capability to catalyse several organic reactions. Thus, surfaces with micrometric patterns have been developed to immobilize functional POM anions. Polymeric substrates have been prepared by breath figure methods with PS/PS-b-PAA blends in order to allow the interaction between acrylic acid groups and different functional POM anions.

Results and discussion: The obtained POM-chitosan nanogels are good candidates for specific drug delivery in breast cancer therapies, since chitosan networks swell at acidic pH, while they remain collapsed at physiological pH. The suitability of these nanocarriers to successfully load and release the POMs in a biological medium have also been evaluated.

The anchoring of the POMs onto the patterned polymeric surfaces have been analysed by ToF-SIM technique. The polyoxovanadates present a good immobilization capability whereas the other POM-based systems studied present difficulties to be suitably incorporated into the functional device.

The authors thank EG/GV (IT718-13; bG18) and MINECO (MAT2017-89553-P) for financial support. Technical and human support provided by SGIKER (UPV/EHU) is gratefully acknowledged

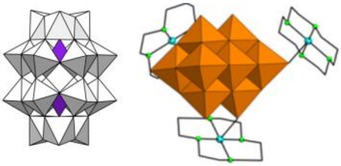

Figure 1: Sturctures of the polyoxometalates used in these studies.

Nanoscale Direct Writing by Near-Field Electrospinning Method

Özge Sağlam

İzmir University of Economics, Faculty of Engineering, Sakarya Cad. 156, İzmir, Turkey
ozge.saglam@ieu.edu.tr

Nanofibers are used as building blocks to enhance the performance of advanced technological devices due to their intriguing physical [1] and chemical properties [2]. Despite numerous nanofiber production methods, the electrospining method [3] is a preferred one due to the continuous production of a wide variety of polymers and high-yield fabrication. In this study, a new type of low-cost nano/micro manufacturing technique, which does not require any advanced facilities or any photo mask as in photolithography technique was implemented. To achieve this, nanofibers were produced by near-field electrospinning technique and written directly on the substrate with an x-y platform. The electrospinning setup includes precisely controlled platform, injector pump, high voltage supplier and a camera. Several parameters were optimized by electrospinning directly on the substrate. The most important factors affecting on the nanofiber patterning are the applied voltage, distance between the needle and the collector, velocity of the stage, concentration of polymer solution and flow rate of the injector. After controlling and optimizing all these variables, the glass substrate was coated by evaporation process and the fibers was directly written on the substrate (Figure 1). The uncovered areas were etched by reactive ion etching. Finally, the nanofibers were stripped off and electrode arrays were obtained. The morphology of electrode arrays was observed by atomic force microscopy and the structure of nanofibers was examined by the scanning electron microscopy.

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Figures

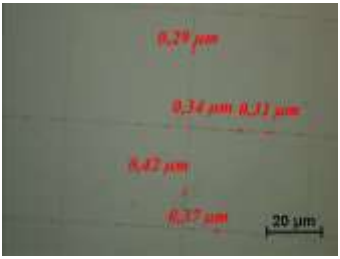

Figure 1: Deposition pattern of fibers formed by near-field elecrospinning method

On-Surface Hydrogen-Induced Covalent Coupling of Polycyclic Aromatic Hydrocarbons via a Superhydrogenated Intermediate

Carlos Sánchez-Sánchez[1], José Ignacio Martínez[1], Nerea Ruiz del Arbol[1], Pascal Ruffieux[2], Roman Fasel[2,3], María Francisca López[1], Pedro de Andrés[1], José Angel Martín-Gago[1]

[1]Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC). Sor Juana Inés de la Cruz 3, 28049 Madrid (Spain).
[2]Swiss Federal Laboratories for Materials Science and Technology (Empa). Ueberlandstrasse 129, 8600 Duebendorf, Switzerland
[3]Department of Chemistry and Biochemistry, University of Bern. Freiestrasse 3, 3012 Bern, Switzerland
cssanchez@icmm.csic.es

The covalent coupling of aromatic molecules via dehydrogrenation reactions is of pivotal importance in organic chemistry, energy, biology, and astrochemistry, to name a few. It is involved in a plethora of processes, ranging from drug synthesis to the formation of polycyclic aromatic hydrocarbons (PAHs) in space. So far, dehydrogenation reactions are based on the utilization of metal catalysts and/or in the previous functionalization of the molecules, both being aspects which can complicate the aimed process. For these reason, it is highly interesting to find a new strategy to covalently bind unfunctionalized PAHs without the presence of a metal catalyst.

Here, we present a novel approach for the activation and subsequent covalent coupling of unfunctionalized polycyclic aromatic hydrocarbons (PAHs) which does not significantly depend on the nature of the surface.[1] This strategy is based on the rupture of the local aromaticity of the molecule induced by the sp^2 to sp^3 hybridization transition taking place upon superhydrogenation of the molecules when exposed to atomic hydrogen. This process results in the formation of a new covalent C-C bond and the release of two hydrogen molecules. This mechanism, which has been characterized by high-resolution STM and rationalized by DFT calculations, opens a door toward the activation and covalent coupling of unfunctionalized PAHs on low reactive surfaces and could explain the formation of larger PAHs in space.

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Figures

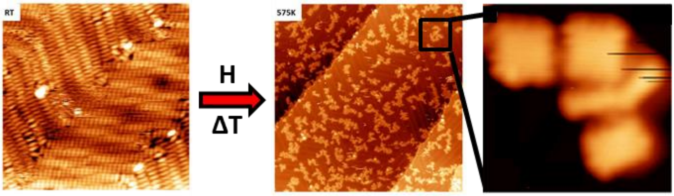

Figure 1: STM images of the Au(111) surface covered by a pentacene layer before (left) and after (middle) annealing the system at 575 K in the presence of atomic hydrogen. Right: nanographenes formed upon exposure to H.

Carbon nanoparticles as cosmic dust analogues

Lidia Martínez[1], **Gonzalo Santoro[1]**, Pablo Merino[1], Mario Accolla[1], Koen Lauwaet[2], Jesús M. Sobrado[3], Hassan Sabbah[4], Ramón Peláez, Victor J. Herrero[5], Isabel Tanarro[5], José Ignacio Martínez[1], Marcelino Agúndez[6], Pedro de Andrés[1], Gary Ellis[7], Christine Joblin[4], José Cernicharo[6] and José A. Martín-Gago[1]

1. Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Cantoblanco, 28049 Madrid, Spain.
2. IMDEA Nanociencia, 28049 Cantoblanco, Madrid, Spain.
3. Centro de Astrobiología (CAB, INTA-CSIC), 28850 Torrejon de Ardoz, Spain.
4. IRAP, Université de Toulouse, CNRS, CNES, 9 Av. Colonel Roche, 31028 Toulouse Cedex 4, France.
5. Instituto de Estructura de la Materia (IEM-CSIC). c/Serrano 123, 28006 Madrid, Spain.
6. Molecular Astrophysics Group, Instituto de Física Fundamental (IFF-CSIC), c/Serrano 113, 28006 Madrid, Spain.
7. Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), c/Juan de la Cierva 3, 28006 Madrid, Spain.

gonzalo.santoro@icmm.csic.es

Cosmic dust is formed in the circumstellar environments of dying stars. In these particular regions of the universe, the accretion from the gaseous phase produces small clusters and nanoparticles which are then ejected to the interstellar medium where energetic processing takes place. In this sense, the fabrication and processing of nanoparticles in the laboratory, at conditions resembling those at the atmosphere of dying stars, constitutes an invaluable tool to understand the chemical complexity in space. To this purpose, we have designed and built a novel ultra-high vacuum machine to simulate in the laboratory the formation of cosmic dust [1].

We have fabricated carbon nanoparticles in the gas phase from carbon atoms and molecular hydrogen using gas aggregation sources. The obtained small carbon clusters and nanoparticles are aliphatic in nature and present a low degree of hydrogenation. Our results suggest that the observed aromatic species in space are not efficiently formed in the circumstellar environments of dying stars but after the processing of the carbon clusters on the surface of cosmic dust grains [2]. These results open new possibilities for interpreting the chemical routes leading to chemical complexity in space and stablish accurate and controlled laboratory simulation experiments as powerful methods for astrophysics.

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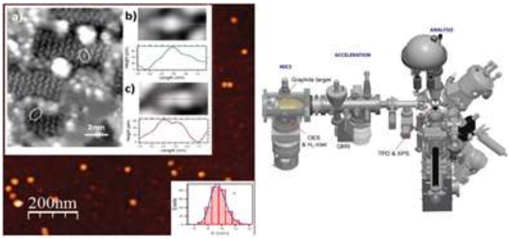


Figure 1: Left: STM and AFM images of C-nanograins and C-clusters collected on a surface. Right: technical drawing of the "Stardust" configuration used in the experiments.

Radical Dendrimers. Synthesis, Characterization and Biomedical Applications

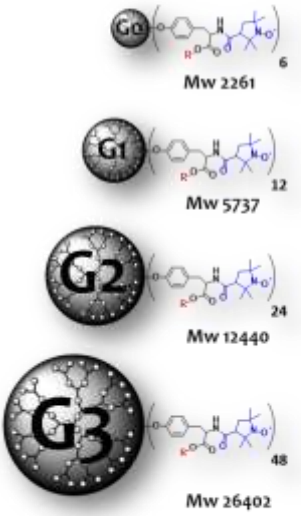
José Vidal-Gancedo, Luiz F. Pinto, Vega Lloveras

Instituto de Ciencia de Materiales de Barcelona – CSIC. Campus UAB, 08193 Bellaterra, Barcelona, Spain and CIBER – BBN, Barcelona, Spain.
j.vidal@icmab.es

Our interest is focused on the study of molecular materials based on radical dendrimers, their magnetic properties as well as their biomedical applications.[1]
Dendrimers are a very special class of hyperbranched macromolecules, which are synthesized step-by-step in order to ensure a good monodispersity. The three-dimensional structure of these molecules proceed from the central core with exponentially increasing number of repeated units and terminal groups.

The term "radical dendrimers" has been used in the case of highly functionalized dendrimers with organic radicals. Here we present a series of several generations of dendrimers built with phosphorus as branching points and with nitroxyl radicals as end groups. The interaction between pendant stable radicals at the exterior of the dendritic surface and their dynamic behaviour can be studied by Electron Paramagnetic Resonance (EPR) spectroscopy. This is important to understand the magnetic properties of these functionalized dendrimers as well as other related ones like relaxivity. The properties of the radical dendrimers depend on the core dendrimer, the size (generation of the dendrimer), the radical and the linker between the kind of radical and the dendrimer branches.

Molecules with many unpaired electrons, which possess high-spin ground state and stability at room temperature, are particularly challenging and promising targets. For example as contrast agents for Magnetic Resonance Imaging as alternative imaging probes to Gadolinium (Gd) and other metal based contrast agents to overcome their established toxicity.



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Spectroscopic kinetic determination of hard protein corona composition

M. Vitali[1], V.F. Puntes[1,2,3]. (1) Institut de Recerca Vall d´Hebron (VHIR). Pg. Vall d'Hebron, 119-129 08035 Barcelona (Spain) (2) Institució Catalana de Recerca i Estudis Avançats(ICREA) Pg. Lluís Companys, 23, 08010 BCN (3) Institut Català de Nanociencia i Nanotecnologia (ICN2), Campus de la UAB, Av. Serragalliners, s/n, 08193 BCN.

michele.vitali@vhir.org

The protein content and composition of the NP protein corona (NP-PC) will determine the interaction of the NP-PC complex with other biological entities in-vivo and in-vitro[1-2]. Current methods for the composition determination, like spectroscopies or Mass Spectrometry[3], rely still on good technical skills and careful manipulation of the materials, and this is the main reason behind the controversies about the final PC composition. Here, we analyse the different profiles of NP-PC corona formation using the two model proteins (albumin and immunoglobulin) to develop a robust and reliable method, mainly based on NP colloidal stability study when the stabilizing protein excess is removed (**Figure 1**), for analysis of the PC formation, evolution and composition, and further compare them to serum. To do that, we employed time dependent UV-Visible absorption spectroscopy, Dynamic Light Scattering, and Z-Potential measurements, providing a simple and reliable approach for determining both density and composition of the resulting hard-PC. We observed different temporal behaviour for the nanoparticle-protein association depending on the affinity of each tested protein for the NP surfaces. Surprisingly, the expected evolution from a non-stable –soft- to stable –hard- protein corona was confirmed for serum and albumin, while immunoglobulin G inevitably and slowly led to nanoparticle aggregations, indicating lower affinity for the NP surface under the tested experimental conditions. Finally, different kinetic profiles allows for composition determination and the study of the kinetic evolution of the protein corona indicates the dominance of albumin. Mass spectrometry analysis of the digested hard-PC confirmed this observation.

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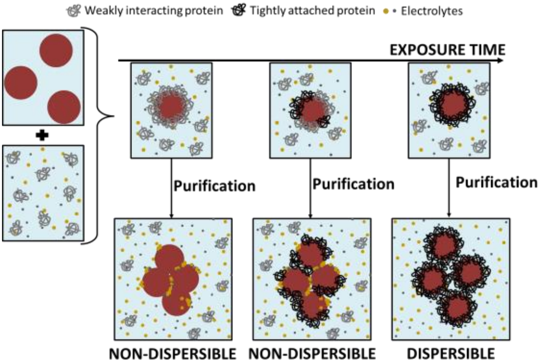

Figure 1: Analysis of the formation and evolution of the NP-PC at different exposure time. The colloidal stability of the NP is determined by UV-Vis spectroscopy and DLS.

Lipase-powered mesoporous silica nanoparticles for triglyceride degradation

Lei Wang[a,b]+, Ana C. Hortelão[a]+, Xin Huang[b] and Samuel Sanchez[a,c]*

[a] Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology (BIST), Baldiri i Reixac 10-12, 08028 Barcelona, Spain

[b] MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

[c] Institució Catalana de Recerca i Estudis Avançats (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

+ These two authors contributed equally to this work.

E-mail: ssanchez@ibecbarcelona.eu

Abstract

The development of synthetic nanomotors for technological applications for life science or nanomedicine is a key focus of current basic research. Enzyme-powered nanomotors offer more advantages, due to their biocompatible and biomimetic properties, capable of actuating in biological systems without side effects[1,2]. Herein, we not only explored another enzyme to the library of biocatalysts with the ability to power motor motion, but also shows an enzymatic motor that retains activity in organic solutions, degrading the triglyceride [3]. The biofriendly propulsion of lipase powered MSNs was realized through the biocatalytic reaction of lipase and its representative water-soluble substrate (triacetin as fuel), exhibiting the enhanced motion (i.e., ~50% increase of diffusion coefficient, Figure 1) at low triacetin concentration (e.g. < 10 mM) compared to Brownian motion, with the lifetime of ~40 min. Particularly, lipase here not only served as the power engine, but also functionalized as a cleaner for the lipid globules (e.g. tributyrin) in PBS solution, which offered a potential tool for dealing with the lipid storage diseases in the biomedical fields.

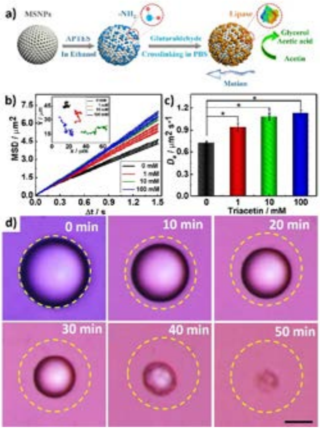

Figure 1. (a) Schematic representation of the functionalization strategy for the preparation of the lipase-based nanomotors whose motion was triggered by catalytic reaction with triacetin. (b) Representative trajectories (inset) of LNMs with different triacetin concentrations of 0 mM (black), 1 mM (red), 10 mM (green), and 100 mM (blue) and corresponding mean-squared displacements (MSD) (n ≥ 20, error bars represent SE); c) effective diffusion coefficients obtained by analysing the MSD for different triacetin concentrations; d) The colour change of the surrounding medium is caused by the litmus indicating the continuous generation of butyric acid. Round dashed circles indicate the initial size of the tributyrin droplets. The scale bar is 5 µm.

Acknowledgements

L.W. thanks the NSFC (No. 51703043), the fellowship under Horizon 2020's Marie Skłodowska-Curie Actions (Grant No. 712754). A.C.H. thanks MINECO for the Severo Ochoa fellowship. S.S. thanks the Spanish MINECO for grants CTQ2015-68879-R (MICRODIA) and CTQ2015-72471-EXP (Enzwim).

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Oral Contributions
PhD Students

Stacked and Overlapped Photonic Structures in Nanoporous Anodic Alumina

Laura. K Acosta, Elisabet Xifre-Perez, Josep Ferré-Borrull, and Lluis F. Marsal

Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, Avinguda Països
Catalans 26, 43007 Tarragona, Spain
lluis.marsal@urv.cat

Nanoporous anodic alumina (NAA) is a promising material formed by the electrochemical anodization of aluminium, a cost effective and fully scalable process compatible with convetional micro and nanofabrication approaches that allows the precise control over the geometry and distribution of the pores [1-2]. The optical properties of NAA rely intrinsically upon its nanoporous architecture. Therefore, to engineer the nanoporous structure of NAA provides novel means of modulating its refractive index in a multidimensional fashion to fabricate advanced materials with unique optical properties to guide, reflect, transmit, emit incident light [3]. The design of photonic structures with innovative architectures and materials can control light–matter interactions at the nanoscale in novel ways. These nanostructures would enable new opportunities to develop advanced materials for many applications, including optical chemical sensing and biosensing [4]. In this work, we present a comprehensive study of diferent photonic structures based on single and multiple periodic structures with sinusoidal profiles in an overlapped and stacked configuration. Figure 1 shows the conceptual illustration of the fabrication and characterization of multiple photonic structures with sinusoidal profile in stacked configuration and their application of photonic structures for the detection of Glucose.

Acknowledgements: This work was supported in part by the Spanish Ministry of Economy and Competitiveness TEC2015-71324-R (MINECO/FEDER), the Catalan authority AGAUR 2017SGR1527, and ICREA under the ICREA Academia Award.

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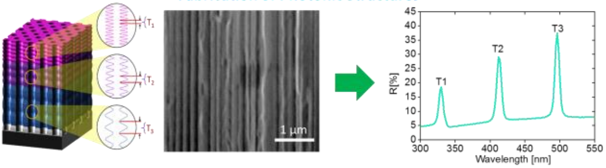
Figures

Fabrication of Photonic Structures



Sensing Application of Photonic Structures

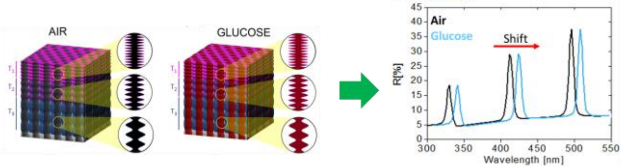


Figure 1: Conceptual illustration of fabrication and characterization of Photonic structures in stacked configuration and sensing application of Photonic Structures with Glucose.

Vertically Aligned Carbon Nanotubes grown on Graphite Paper Electrodes for Highly Flexible Supercapacitors

Islam Alshaikh[1,2], Roger Amade[1,2], Fernando Pantoja-Suárez[1,2,3], Enric Bertran-Serra[1,2]

[1]FEMAN Group, Dep. Applied Physics, Universitat de Barcelona, C/Martí I Franquès, 1, 08028 Barcelona, Spain
[2]Institute of Nanoscience and Nanotechnology, Universitat de Barcelona.
[3]Department of Materials, Escuela Politécnica Nacional, Ladrón de Guevara, E11-253, Quito, Ecuador
iralshaikh@ub.edu

Abstract

Carbon nanotubes (CNTs) are being extensively investigated for electrochemical applications. Among the multiple techniques used to grow the CNTs for specific applications, like supercapacitor electrodes, we have precisely tuned the parameters of plasma enhanced chemical vapor deposition (PECVD) for growing vertically aligned CNTs (VACNTs), each one electrically connected to a 0.20 mm thick and highly flexible PAPYEX® graphite foil N998. Iron (Fe) thin film was used as a catalyst to grow the CNTs. Catalyst thickness, annealing temperature and PECVD time were also explored. Optimum conditions were found to be 2 nm of Fe film thickness, 750°C of annealing temperature and 15 min of PECVD process. To increase the hydrophilicity and to remove the amorphous carbon generated during the deposition of the CNTs, samples were treated by O_2 plasma. Raman spectra showed that the CNTs become more crystallyne after functionalization with O_2 plasma (Figure 1). Electrochemical characterization was carried out for the obtained CNTs. MnO_2 nanoparticles were deposited on the CNTs (Figure 2) to increase the areal capacitance from 22.5 mF/cm^2 to 40.2 mF/cm^2 at a scan rate of 10 mV·s^{-1}.

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Figures

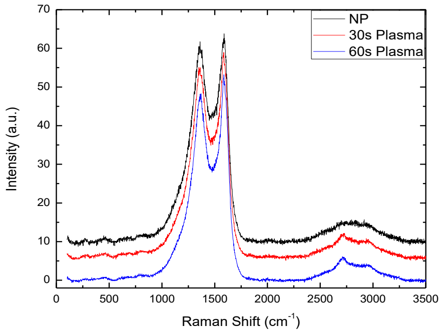

Figure 1: Raman specta of CNTs over graphite paper before and after O_2 functionalization.

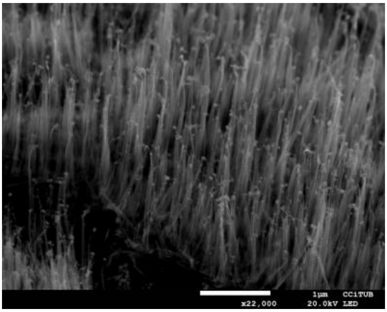

Figure 2: SEM image of VACNTs over graphite paper.

Preparation of rosemary essential oil-loaded multiple lipid nanoparticles (RO-MLNs) and evaluation of their antibacterial activity

Ben Khalifa Rayhane[1], Soraya Rodriguez Rojo[2], Frédéric Gaspar[3], Chekir-Ghedira Leila[1]
[1] Laboratory of Cellular and Molecular Biology, Faculty of Dental Medicine, University of Monastir, Avenue Avicenne, 5019 Monastir, Tunisia, benkhalifarayhane@yahoo.com; leila.chekir@laposte.net.
[2]BioEcoUVa, Institure of Bioeconomy. High Pressure Processes group, School of Industrial Engineering, University of Valladolid, Spain, soraya.rodriguez@uva.es.
[3] iBET – Instituto de Biologia Experimental e Tecnológica, Food & Health Division, Food Safety and Microbiology Laboratory, Apartado 12, 2781-901 Oeiras, Portugal, fgaspar@ibet.pt.

Introduction:

Antibacterial resistance has emerged as one of the major threatens for public health in this century mainly due mainly to antibiotic (ATB) misuse in human medicine but also in farming [1]. The combined use of ABTs with other natural antimicrobial agents, such as essential oils (EOs),provides a promising solution towards combating multidrug resistant (MDR) bacteria [2].

Owning to the failure of antibiotic therapy and the limitations of industrial applications of EOs despite their numerous biological and medicinal properties, the co-nanoencapsulation of EOs with ATBs seems to be apromising strategy to protect the active molecules against their degradation, to improve their bioavailability and their stability during the treatment and storage processes. Currently, numerous methods of encapsulation of EO have been studied and a series of more complex and structured emulsions have been developed. One of the systems that is getting increased attention in the last decade is the multiple lipid nanoparticles (MLNs) since they combine the advantages of water-in-oil-in-water (W/O/W) multiple emulsions and solid lipid nanoparticles (SLNs) to be able to co-encapsulate an EO and a hydrophilic antibiotic.

The objective of this research is to prepare a MLN suspension of pure Rosemary EO (RO-MLN) to evaluate its antimicrobial activity against MDR strain of *Pseudomonas aeruginosa*.

Methods

MLN are produced by a two step process based on melt-emulsification technique combined with ultrasonication as described elsewhere [3-5].The selected lipids are the solid glyceryl tristearate (GTS) and the liquid glyceryl trioleate (GTO). Pluronic L64 and Tween 80 were used as surfactants in the primary and secondary emulsions, respectively. The effect of different parameters in the encapsulation efficiency, particle size distribution and physical stability was studied. Regarding the primary water in oil (w/o) emulsion, the GTS was fixed at 10%, based on preliminary experiments, while varying the % EO in the liquid lipid mixture from 20% to 100%. Also the ratio of the first emulsion to the second water phase was varied from 20 to 40%. Finally, the effect of both surfactant concentrations was analyzed in the range from 0 to10% for primary emulsion and 0 to 5% for secondary emulsion

The antibacterial activity was carried out following the microdilution method using different strains of *P. aeruginosa* resistant or not to the antibiotics.

Results

The optimized RO-MLN formulation exhibited a monomodal particle size distribution with a mean particle size of 110 nm and a span <1 and encapsulation efficiency up to 90%, determined by GC-MS. RO-MLN was physically stable for at least 30 days thanks to its high negative zeta potential (> -60 mV).

The antibacterial test against susceptible and resistant strains of *P.aeruginosa* showed that RO-MLN had 6 times more antibacterial activity than the pure essential oil, which suggests that converting the essential oil to nano-scale particles improved its bacteriostatic activity.

Conclusions

The current study revealed that the RO-MLN can be considered as a new strategy to fight against bacterial multidrug resistance. The antibacterial activity could be further improved with the co-encapsulation of a drug antibiotic, such as cefepime, an aqueous soluble antibiotic.

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Tip-selective functionalization of gold nanorods with dye-labeled DNA's for effective fluorescence enhancements

David Botequim,[1,2] Inês I. R. Silva,[1] Duarte M. F. Prazeres,[2] Sílvia M. B. Costa[1] and Pedro M. R. Paulo[1]
[1]Centro de Química Estrutural, and [2]iBB – Institute for Biotechnology and Bioengineering
Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais 1, 1049-001 Lisboa, Portugal
davidbotequim@tecnico.ulisboa.pt

Metal nanoparticles can act as optical antennas, coupling light more efficiently in the excitation and emission from fluorophores [1]. Their antenna effect has been explored for the development of plasmon-enhanced fluorescence biosensors, in which molecular recognition events are detected by fluorescence signals with intensified response [2]. In non-spherical particles, large fluorescence enhancements are obtained in surface regions where large near fields, or plasmon hot-spots, occur. Typically, these hot-spots are located in regions of large curvature, e.g. at the tips of gold nanorods (Figure 1A). In this contribution, colloidal gold nanorods were functionalized with dye-labeled oligos to optimize antenna effects for fluorescence signal enhancement. A tip-selective functionalization was implemented in order to specifically attach the fluorescent oligos at the plasmonic hot-spots. This approach afforded fluorescent dye-particle assemblies with a 15-fold increase in steady-state emission relatively to the same dye in the absence of the nanorod antenna (Figure 1B). As comparison, a non-selective functionalization of the gold nanorods produced highly loaded dye-particles, but without an effective fluorescence enhancement (Figure 1C). Dye-particle conjugates were further characterized by confocal fluorescence lifetime microscopy with single-particle sensitivity. The results reported here highlight the importance of site-selective approaches for hot-spot functionalization, maximizing plasmonic effects for applications in imaging or biosensing [3]. The gold nanoantennas developed have potential for nucleic acid detection using DNA-based receptors, since improved responses would allow achieving lower detection limits and increased sensitivity.

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Figures

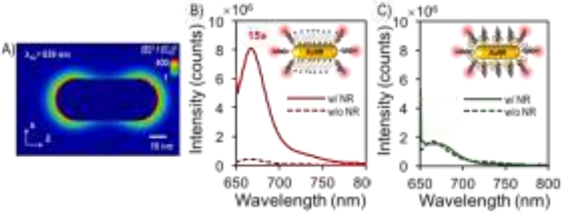

Figure 1 – A) Plasmon-enhanced near field map calculated for a gold nanorod (60 nm x 25 nm) excited at 639 nm. B and C) Fluorescence spectrum of dye-labeled oligos on gold nanorods (filled lines) and without nanorods (dashed lines) in aqueous solution excited at 640 nm. In the tip-selective functionalization, a fluorescence enhancement of 15-fold increase of emission was observed (B), while in the non-selective functionalization it is not observed enhancement (C).

Chiral plasmonic systems: Assembling of achiral building blocks into 3D nanostructures

Carolina de Dios, Alba Jiménez, Fernando García, Antonio García, Alfonso Cebollada and Gaspar Armelles
IMN-Instituto de Micro y Nanotecnología de Madrid (IMN-CSIC),
Isaac Newton 8, PTM, Tres Cantos, Madrid, 28760, Spain
gaspar@imm.cnm.csic.es

Plasmonic nanostructures that exhibit chiral properties have become a subject of interest in recent years due to their applications in spectroscopy, catalysis and ultrasensitive detection of chiral molecules **[1]**. In the present work, we investigate the effect on the optical properties (lineal (LD) and circular dichroism (CD)) of individual achiral nanorods by adding non-chiral elements to the structures. Firstly, we show the evolution of the chiral properties by adding pillars according to their composition (Au and CaF_2) and their arrangement with respect to the rods (*Figures 1 and 2*). In addition we incorporate ferromagnetic materials in order to analyse the intertwined magneto-optical and chiral properties and control them by magnetic fields **[2]**. Finally, we explore the effect on the optical response of the structures by attaching a second rod. We analyse the role of the interactions in stacked gold dimers by modifying the dielectric separator and the relative angle between the rods **[3]**.Nanostructures were fabricated by Hole-mask colloidal lithography (HCL).This fabrication method allows growing nanostructures with a controlled chirality and handedness of the structure over cm^2 **[4]**. AFM and SEM images were used to characterize the morphology of the structures. Optical characterization was carried out by measuring Mueller Matrix elements to discriminate the chiral effect from the optical anisotropy, and magneto-optical Kerr measurements in polar configuration to analyse the magnetic contribution in their magneto-optical properties.

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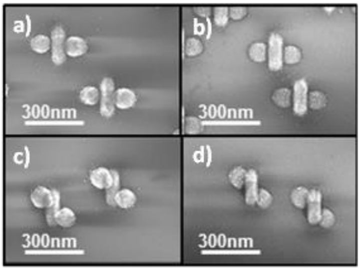

Figure 1: SEM images of individual nanorods with pillars at different configurations and composition (Au (**a)** and **c)**) and CaF2 (**b)** and **d)**).

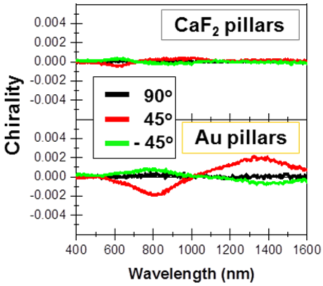

Figure 2: Spectra representing the chiral optical responses obtained from the Mueller Matrix elements according the composition of the pillars [CaF2 pillars **a)** and Au pillars **b)**] and the angle pillars-long optical axis of the rods.

Controlled fabrication of nanotubes from nanoporous anodic alumina

Jakub T. Domagalski, Elisabet Xifre-Perez, Josep Ferre-Borrull, Lluis F. Marsal*

Universitat Rovira I Virgili, Avinguda dels Països Catalans, 26, 43007 Tarragona, Spain.
* Lluis.marsal@urv.cat

Recent decades brought significant advances in the field of nanoporous materials. High surface area, well-defined pore size and functionalization possibilities are just a few of many features making nanoporous materials attractive in broad range of applications like catalysis, biomaterials and template to fabricate different nanostructured materials. Electrochemical anodization of aluminium is affordable and effective method to fabricate nanoporous structures made of anodic alumina. Tuning parameters of the process like voltage, current, electrolyte used and duration of the process, structures varying in shape and size can be synthesized [1]. Growing knowledge about effects of different parameters on characteristics of obtained structure led to design of more sophisticated fabrication methods, leading to creation of complex structures like nanopillars, funnels or rugate structures [1-3].

In this communication, we present fabrication of hollow-inside anodic alumina nanotubes. Pulse anodization is performed in galvanostatic conditions, consisting of interlacing high- and low current density pulses. Such structure is subjected to etching in mixture of $CuCl_2$ and HCl in order to remove remaining aluminium and weaken connection between individual layers of structure, followed by gentle sonication in water to liberate nanotubes. Fabricated nanoparticles present low dispersity of size and their lenght can be tuned adjusting pulse anodization parameters [4]. Due to inert character of alumina and optical properties, such nanoparticles may find application in fields like biomaterials or photonics [4,5].

Acknowledgements: This work was supported in part by the Spanish Ministry of Economy and Competiveness TEC2015-71324-R (MINECO/FEDER), the Catalan authority AGAUR 2017-SGR-1527, and ICREA under the ICREA Academia Award. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 713679 and from the Universitat Rovira I Virgili (URV).

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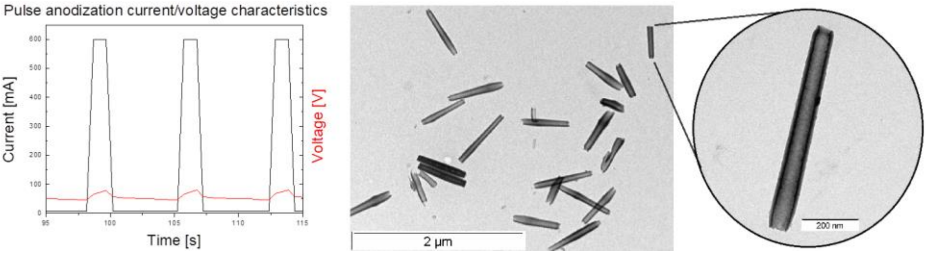

Figure 1: From the left: Current/voltage over time characteristic for galvanostatic pulse anodization, TEM image of water suspension containing anodic alumina nanotubes and magnified image of singular nanoparticle.

Self-Reducible Copper Complexes for Printing on 2D and 3D Heat Sensitive Objects

Yousef Farraj, Shlomo Magdassi

Casali Center of Applied Chemistry, Institute of Chemistry and Center for Nanoscience and Nanotechnology, The Hebrew
University of Jerusalem, Jerusalem 91904, Israel
Yousef.farraj@mail.huji.ac.il

Direct printing of electrical contacts using silver particles inks has gained much interest recently. This approach opened the window for both fast prototyping, and Roll-to-Roll fabrication of various electronic devices, such as RFID tags, touch screens and flexible displays. However, the high cost of silver limits the fabrication of low-cost plastic devices, therefore there is a need to find a replacement. The most promising material is copper, having the second lowest resistivity of metals (only 5% less than silver), and its cost is about 90 times lower. Nevertheless, the main obstacle in utilizing inks containing copper nanoparticles is the rapid oxidation of the particles before and after printing.

Here we describe the formation and utilization of a copper complex ink that undergoes decomposition to yield copper nanoparticles. The ink is stable at ambient conditions, as compared to what is usually encountered in nanoparticles-based inks, such as aggregation and formation of copper oxide. The copper complex undergoes a self-reduction process to pure copper via a decomposition process. The formation of copper nanoparticles, analysis of decomposition process and film formation were evaluated using a variety of analytical tools. Finally, printed patterns were obtained on 2D and 3D substrates as can be seen in Figure 1.

Figures

Figure 1: Ink-Jet printed copper pattern on PET film (left), and on 3D printed plastic object (right)

Hybrid self-assembly of quantum dots and gold nanoparticles driven by protein pairing

M. Fernandez[1], A. Urvoas[2], M. Valerio-Lepiniec[2], A. Burel[3], P. Minard[2], E. Durjardin[4], P. Even-Hernandez[1] and V. Marchi*[1]
[1]University Rennes 1, Institut of Chemical Sciences, UMR 6226 CNRS, Campus Beaulieu, F- 35042 Rennes, France
[2]I2BC, Univ Paris Sud, CNRS, CEA UMR 9198, Bât. 430, F-91405 Orsay, France
[3]Biosit: Biologie, Santé et Innovation Technologique CNRS : UMS 3480, INSERM, Rennes, France
[4]Groupe NanoSciences-CEMES, CNRS UPR 8011, 29 rue J. Marvig, B.P. 94347, F-31055 Toulouse, France
*valerie.marchi@univ-rennes1.fr

The broad field of nanotechnology has resulted in the design of hybrid nanomaterials featuring exclusive properties such as sensing, data or energy storage and biocide activity. Molecule-driven self-assembly of biomolecules led to the design of colloidal assemblies thanks to the direct recognition of specific molecular partners grafted onto nanoparticles. Direct coupling of nanoparticles has been achieved using DNA strands hybridization, peptide coupling or archetypal protein interactions. In this context, assemblies of gold nanoparticles were designed using a pair of artificial α-Repeat proteins (Figure 1a) of high affinity exhibiting a dissociation constant in the nanomolar range.[1,2] These promising proteins induce the self-assembly of complementary colloids in a controlled manner, whilst providing a control on the interparticle distance.

Here we present the design of αRep proteins driven self-assemblies of semiconductor nanoparticles and gold nanoparticles. First, fonctionnalization of the nanoparticles is achieved exchanging an initial polycystein peptidic ligands at the surface of the NP with the αRep proteins.[3] The efficiency of the protein grafting was demonstrated by agarose gel electrophoresis. The molecular recognition properties of the protein-functionalized nanoparticles are evidenced using Surface Plasmon Resonance technique. The selective formation of large colloidal assemblies (Figure 1b) of complementary nanoparticles is demonstrated by transmission electronic microscopy (Figure 1c) and finally characterized by fluorescence spectroscopy. These results open the route to the design of hybrid colloidal assemblies with original optical response.

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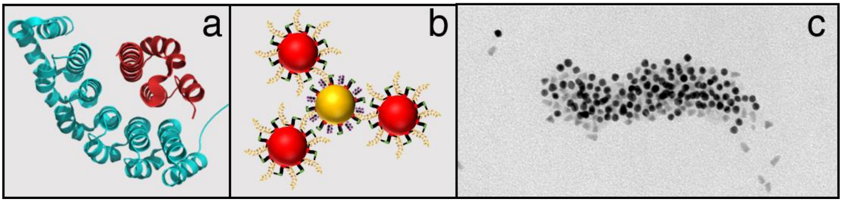

Figure 1: (a) The structure of the pair of artificial α-Repeat proteins used in this work. (b) Schematic representation of the hybrid self-assembly between gold nanoparticles and quantum dots. (c) TEM image of the obtained hybrid nanostructures.

Resistive Switching of $SrIrO_3$ thin films in the vicinity of a Metal Insulator Transition

V. Fuentes[1], B. Vasić[2], Z. Konstantinović[2], B. Martínez[1], Ll. Balcells[1], A.Pomar[1]

1 Instituto de Ciencia de Materiales de Barcelona, ICMAB-CSIC, Campus de la UAB, Bellaterra 08193, Spain

2 Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

vfuentes@icmab.es

The relation between Metal Insulator Transitions (MIT) and Resistive Switching (RS) is important from the fundamental point of view, but also highly relevant because of the possible applications of RS based devices in non-volatile memories [1]. We studied RS of 5d $SrIrO_3$ thin films in the vicinity of a MIT triggered by the reduction of thickness [2]. RS was studied for two characteristic cases: 1. in a thick film which behaves like a semimetal, and 2. in a very thin film which has undergone the MIT and is in an insulating state (see Figure 1). Local electrical properties were measured by means of Conductive Atomic Force Microscopy (C-AFM). In the case of very thin and initially insulating films, I/V curves presented an abrupt increase of the current intensity only for high enough sample voltage indicating a sharp transition into low resistance state (LRS). On the other hand, in the case of initially semimetallic films, this transition was less pronounced without clear threshold voltage for the switching into LRS (see Figure 2). As a result, such different behavior indicates that the MIT has indeed a high impact on the RS. Possible mechanisms of RS in both samples involving oxygen vacancies will be discussed.

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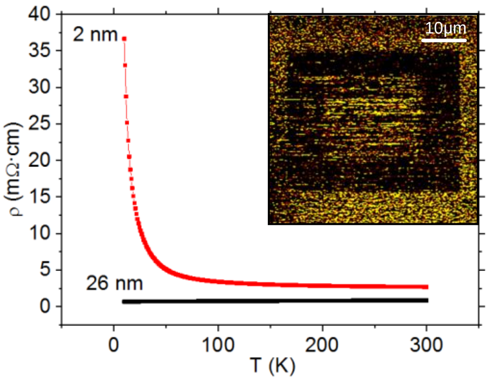

Figure 1: MIT triggered by the reduction of thickness.

Inset: C-AFM current map with a region in the High Resistance State (dark) and a region in the Low Resistance State (inner bright square).

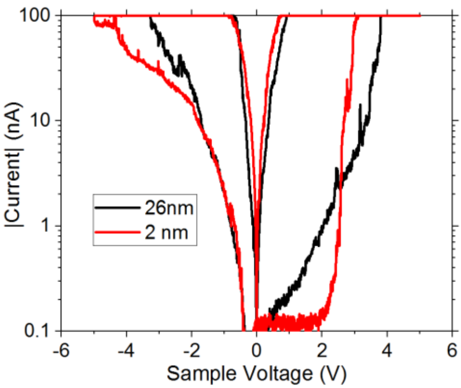

Figure 2: I/V RS curves of 2 nm and 26 nm $SrIrO_3$ thin films.

Comparison of oxidase activity of CeO_2 nanoparticles against laccase enzymes

Dmitry Galyamin[1], Neus G. Bastús[2], Jordi Piella[2], Juan Pablo Esquivel[1], Victor Puntes[2,3,4], Neus Sabaté[1,3]

1 Instituto de Microelectrónica de Barcelona, IMB-CNM (CSIC) C/ dels Til·lers, Campus Universitat Autònoma de Barcelona (UAB), Bellaterra, Barcelona, Spain
2 Institut Català de Nanociència i Nanotecnologia (ICN2), CSIC, The Barcelona Institute of Science and Technology (BIST), Campus UAB, Bellaterra, Barcelona, Spain.
3 Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain.
4 Vall d'Hebron Institut de Recerca (VHIR), 08035, Barcelona, Spain.
dmitry.galyamin@imb-cnm.csic.es

Nanozymes are defined as "nanomaterials with enzyme-like characteristics" [1]. The interest for them is growing as they present lower cost and higher stability in comparison with natural enzymes. Four types of redox enzymes had been mimicked by nanozymes: peroxidase, oxidase, catalase and superoxidedismutase (SOD) [2]. In biosensing applications catalases have been extensively characterized. However, as they need H_2O_2 as a substrate their application in point-of-care devices is not straight-forward. In this sense, oxidase – like nanozymes allows to think in a better solution simplicity as they can catalyze the oxidation of a substrate with the assistance of molecular oxygen dissolved in the solution. A lot of examples of this kind of activity in nanozymes has been reported, among them, ceria nanoparticles (CeO_2-NPs) is a particular interesting candidate that has proved to be able to operate in that mode. However, despite the numerous studies with CeO_2-NPs as oxidase published up to date, the comparison of the response between this nanozyme and natural oxidase-enzyme as laccase has been scarcely studied up to date.

In this work, a comparison of the oxidase activity both CeO_2-NPs and laccase is presented. Ferrocyanide ($K_4[Fe(CN)_6)]$) has been chosen as a mediator. We perform a steady-state kinetic assay at fix concentration of substrate and different concentrations of two different batches of Laccase (A and B) and CeO_2-NPs ranging from $5 \cdot 10^{-4}$ to 0.2 mg/mL. Absorbance measurements were done by recording the 420 nm peak increase in time corresponding to the oxidation of the mediator. Figure 1A shows the obtained results at different times (10 and 60 minutes). It can be seen that the amount of oxidized substrate in time depends on laccase batch. Under the same conditions, nanoceria showed a lower response than its living competitors. In order to compare the different catalytic performances, we characterized the enzymatic activity of the two different batches of laccases and the CeO_2-NPs. After that, we normalized the catalytic response of both laccases and CeO_2-NPs displayed in figure 1B to enzymatic units. It can be seen that both laccase batches and ceria align on the same response curve that follow the same behavior suggesting that under the given conditions, nanoceria perfectly mimics the behavior of a laccase enzyme.

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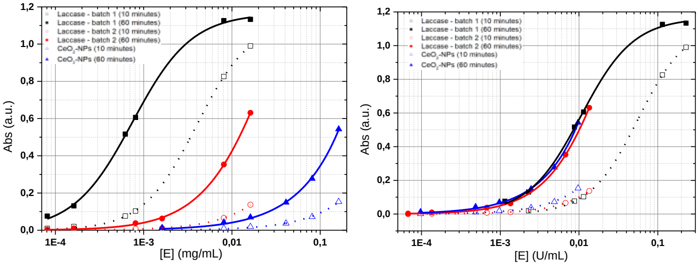

Figure 1: Effect of CeO_2-NPs or Laccase on the kinetics of ferrocyanide (420 nm) oxidation. A: Expressed in mg/mL. B: Expressed in (U/mL)

High-yield spin devices with a long spin lifetime in chemical vapor deposited graphene

Z. M. Gebeyehu , S. Parui, J. F. Sierra, M. Timmermans, M. J. Esplandiu, K. Garello, M. V. Costache and S. O. Valenzuela

Catalan institute of nanoscience and nanotechnology,
08193 Bellatera, Barcelona, spain
zewdu.messele@icn2.cat

Abstract

We demonstrate a high-yield fabrication of non-local spin valve devices with room-temperature spin lifetimes of up to 3 ns and spin relaxation lengths as long as 9 µm in platinum-based chemical vapor deposition (Pt-CVD) synthesized single-layer graphene on SiO_2/Si substrates. The spin-lifetime systematically presents a marked minimum at the charge neutrality point, as typically observed in pristine exfoliated graphene. However, by studying the carrier density dependence beyond $n \sim 10^{13}$ cm^{-2}, it is found that the spin lifetime reaches a maximum and then starts decreasing, a behavior that is reminiscent of that predicted when the spin-relaxation is driven by spin-orbit interaction. The spin lifetimes and relaxation lengths compare well with state-of-the-art results using exfoliated graphene on SiO_2/Si, being a factor two-to-three larger than the best values reported at room temperature using the same substrate [1]. As a result, the spin signal can be easily measured across 30-µm long graphene channels. These observations indicate that Pt-CVD graphene is a promising material for large-scale spin-logic applications.

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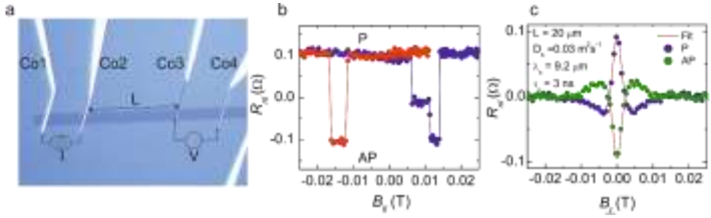

a, Optical image of a CVD graphene non-local spin device **b,** Non-local resistance R_{nl} *as a function of an in-plane magnetic field $B_{||}$ **c**, Spin precession measurements

NanoReg2 Grouping Approach

Paloma Gómez-Fernández
Anna Giusti, Rambabu Atluri, Rositsa Tsekovska, Agnieszka Gajewicz, Margarita D. Apostolova, Chiara L. Battistelli, Eric A.J. Bleeker, Cecilia Bossa, Jacques Bouillard, Maria Dusinska, Roland Grafström, Maciej Gromelski, Yordan Handzhiyski, Nicklas Raun Jacobsen, Paula Jantunen, Keld Alstrup Jensen, Agnieszka Mech, José Maria Navas, Penny Nymark, Agnes G. Oomen, Tomasz Puzyn, Kirsten Rasmussen, Christian Riebeling, Isabel Rodriguez-Llopis, Stefania Sabella, Juan Riego Sintes, Blanca Suarez-Merino, Speranta Tanasescu, Håkan Wallin and Andrea Haase

Gaiker, Parque Tecnológico, Ed. 202 - Zamudio – Bizkaia - Spain,
gomezp@gaiker.es

There is a vast and expanding array of Manufactured Nanomaterials (MNMs) that have unique physicochemical properties. The safety assessment of all those MNMs is time consuming, uneconomical and unethical. Read-across and grouping approaches are used to predict and characterize hazards from substances with structural similarity for which there is not enough experimental data. The EU Horizon 2020 NanoReg2 project has focused to establish MNM grouping strategies in order to tests its applicability for predicting hazard in an explorative read-across approach. The strategy builds on the Marina approach (what they are, where they go, what they do) and extends it on including physical hazards and ecotoxicity and using in vitro strategies for establishing groups. NanoReg2 selected a panel of three cases studies (TiO_2, ZnO and SiO_2) different endpoints. Lack of data was the more pressing problem and a gap filling exercise undertaken, moreover, several physicochemical parameters from the different MNMs were characterized not only as pristine materials but also in biological media in order to assess the specific interactions between MNMs and proteins. NanoReg2 approach also included computational tools during the process. In this presentation, the grouping approach developed as well as all the lessons learnt within this project will be explained for the contribution of future upcoming studies and strategies.

Acknowledgment

NanoReg2 has received funding from the European Union's Horizon 2020 research and innovation programme under grand agreement no. 646221

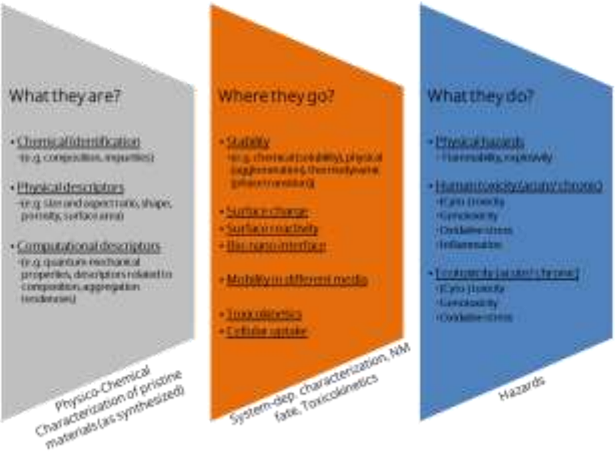

Figure 1: Schematic overview of the NanoReg2 grouping approach.

Ferromagnetic Resonance and Inverse Spin Hall Effect in Permalloy/Pt bilayers

Sergi Martín-Rio, Lluís Balcells, Alberto Pomar, Carlos Frontera, Benjamín Martínez

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, Barcelona, Spain
smartin2@icmab.es

The temperature dependence of magnetodynamical physical effects such as Spin Pumping and Inverse Spin Hall effect (ISHE) has been measured in a set of Py/Pt bilayers as a function of the Pt thickness. Additionally, important physical parameters such as Gilbert damping, saturation magnetization and anisotropy field have been determined as well. We found that the Gilbert damping follows a non-monotonic behaviour with temperature (**Fig. 1**), as reported in other systems [1]. Previous measurements on the temperature dependence of Spin Pumping and ISHE [2] in this system have the serious drawback of requiring the use of complex fabrication process to prepare the samples. In this work we present an easy-to-implement ferromagnetic resonance (FMR) setup for measuring all those effects and parameters straightforwardly. We found that the amplitude of the FMR absorption curves is constant from room temperature to approximately 100K and then it starts to decrease. Because of this reduction, it is of major relevance to normalise the measured ISHE voltage with the FMR absorption amplitude in order to obtain physically coherent results. The resulting normalised ISHE voltage, depicted in **Fig. 2**, follows an inverse linear relation with temperature.

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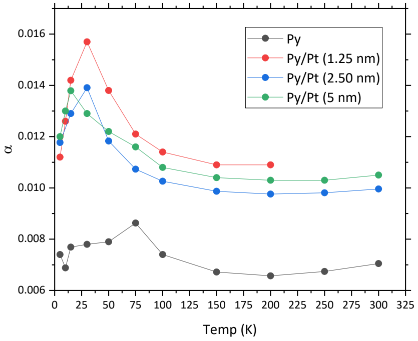

Figure 1: Temperature dependence of the Gilbert damping of the Py/Pt system as a function of the Pt layer thickness.

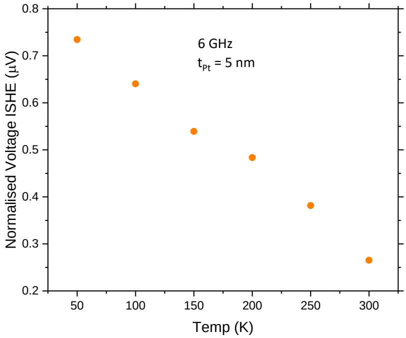

Figure 2: Temperature dependence of the normalized ISHE in a Py (20nm)/Pt (5nm) bilayer at 6 GHz.

Electrochemical Method for Removing Thick Barrier Layer in Nanoporous Anodic Alumina

M.P Montero-Rama, A. Viterisi, C. Eckstein, J. Ferré-Borrull and L.F Marsal*

Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, Avinguda dels Països Catalans, 26, 43007 Tarragona, Spain.
Lluis.marsal@urv.cat

Nanoporous anodic alumina (NAA) has attracted a great deal of interest in the last decades because of its wide range of applications. The main properties of NAA are its chemical stability, its mechanical durability, the cost-effective, easily up-scalable production process and the possibility to taylor nanopore sizes and interpore distances over a very wide range of values. As the NAA is obtained by anodization of aluminium foils, we can use the aluminium foil as an electrical back contact. However, since the NAA presents a thick barrier layer at the bottom side, we need to remove this barrier layer to obtain a good electrical contact.[1] In this work, we present a new method to remove this barrier layer. Self-ordered array of nanopores was obtained using the 2 steps anodiazation[2,3]. Following a partially etching in phosphoric acid was performed and a re-anodized step was carried out at constant current.[4] This results in the formation of several nanoscopic channels in the barrier layer, which lead to its complete removal upon a final chemical etching step, remaining intact the pore structure and obtaining an electrical back contact.

Acknowledgements: This work was supported in part by the Spanish Ministry of Economy and Competitiveness TEC2015-71324-R (MINECO/FEDER), the Catalan authority AGAUR 2017SGR1527, and ICREA under the ICREA Academia Award.

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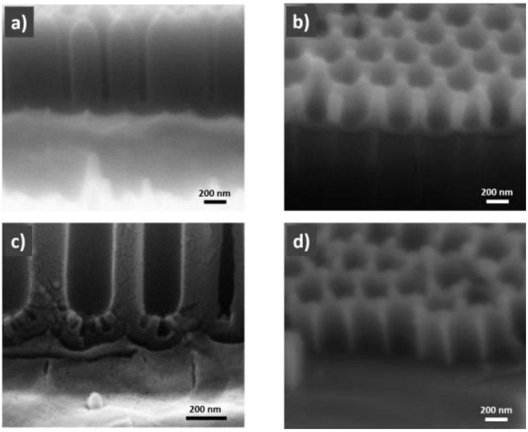

Figure 1: Cross-section views SEM of a phosphoric NAA **a)** after the two step anodization. **b)** after the partial pore widening. **c)** after re-anodization at constant current. **d)** after final pore widening. Sacles are indicated in the pictures.

Synthesis, thermal sensing and photothermal conversion efficiency of Ho,Tm:Y_2O_3 colloidal nanocrystals with different morphologies

Albenc Nexha, Joan J. Carvajal, Maria Cinta Pujol, Francesc Díaz, Magdalena Aguiló
Universitat Rovira i Virgili, Departament Química Física i Inorgànica, Física i Cristal·lografia de Materials i Nanomaterials (FiCMA-FiCNA) – EMaS, Campus Sescelades, E-43007, Tarragona, Spain
albenc.nexha@urv.cat

Yttrium oxide (Y_2O_3) possesses interesting properties such as a broad transparency range (0.2-8 µm) with a band gap of 5.6 eV, high thermal conductivity, high refractive index and low phonon energy, which have made it an attractive choice as host material for lanthanide (Ln) ions for optical applications.[1,2] However, the majority of applications developed up to now have been designed to the bulk Y_2O_3 materials. In this work, we evaluate the properties as luminescent nanothermometers and photothermal agents of the Ho,Tm: Y_2O_3 doped nanomaterials with different morphologies.

Cubic Y_2O_3 colloidal nanocrystals were synthesized via the thermolysis reaction, incorporating the dual role of two organic surfactants (oleic acid and oleylamine) and the non-coordinating agent 1-octadecene. Y_2O_3 nanocrystals with different morphologies ranging from nanospheres, broken-edges-planar triangles, fully planar triangle, heart-like and nanowires-to-rods structures were synthesized. The different morphologies were obtained by incorporation of different additives, such as $NaNO_3$ and NaCl. All the nanocrystals obtained were characterized structurally, demonstrating that in all cases pure body-centered cubic (bcc) Y_2O_3 with spatial group *Ia*-3 was produced. Possible mechanisms for the production of such different morphologies will be discussed.

The nanocrystals were doped with Ho^{3+} and Tm^{3+}, without observing any disturbance on the structure or morphology of the samples due to the presence of dopants. They were tested as luminescent nanothermometers operating in the short-wavelength infrared (SWIR) region via excitation at near infrared (808 nm). The light-to-heat conversion efficiency of the nanocrystals was also studied by the method on the integrating sphere. The potential use of these nanocrystals as self-assessed photothermal agents for hyperthermia applications will be discussed, taking into account the effect of the different shapes of the nanocrystals.

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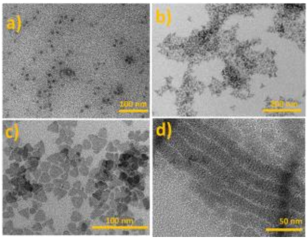
Figure 1: Y_2O_3 colloidal nanocrystals with different morphology: a) nanospheres, b) broken-edge triangle, c) heart like and d) nanowires-to-rods like



Aknowledgement: This work has been supported by Spanish Government under project MAT2016-75716-C2-1-R (AEI/FEDER, UE) and by Generalitat de Catalunya under project 2017SGR755 and 2017FI_B 00620, 2018FI_B1 00161.

Temperature-responsive magnetic logic gates in cellular hyperthermia process

Rui Oliveira-Silva,†‡ Rute A. Pereira,† Fábio M. Silva,† Vítor M. Gaspar,†
Alfonso Ibarra,§ Angel Millán,‖ Filipa L. Sousa,† João F. Mano,† Duarte M. F. Prazeres,‡ and Nuno J. O. Silva,†
† CICECO Aveiro Institute of Nanotechnology, Universidade de Aveiro
‡ Instituto de Bioengenharia e Biociências (IBB), Departamento Bioengenharia, Instituto Superior Técnico
§ LMA, Instituto de Nanociencia de Aragón, Universidad de Zaragoza.
‖ Instituto de Ciencia de Materiales de Aragón, CSIC - Universidad de Zaragoza.
Ruipsilva@tecnico.ulisboa.pt

The Biomolecular Big Brother can be described as the ability to control and monitorize biological processes, which can ultimately increase the potential of Personalized medicine. In this regard sensors for continuous monitoring of temperature have been used during cellular hyperthermia processes. However, an answer to the question "did the system locally exceed a certain threshold temperature?" can be more accurate and useful. Acknowledging this, we developed[1] a system capable of recording temperature fluctuations above a defined threshold. This system uses hard magnets of iron selenide (Fe_3Se_4) nanoplatelets, which can retain magnetic moment in the absence of an applied magnetic field. Additionally, the magnetic phase transition of iron selenide nanoplatelets occurs at a defined temperature (Tc) slightly above room temperature and can be modulated by tunning their size and/or crystallinity. Thus, at temperatures below Tc, the nanoplatelets can be set to a well-defined magnetization that will remain unchanged until the temperature crosses above the Tc.

New iron selenide nanoplatelets with great control over size and, consequently, Tc between 0 and 60 ºC were developed by improving methods from literature. Nanoplatelets with Tc tuned to 42 ºC were applied in cellular hyperthermia assays using prostate cancer cells (PC-3 line) that were subjected to different thermal doses. For lower thermal doses (470 mW/cm^2) the threshold of 42 ºC was not crossed and most cells appeared to be viable, whilst for high thermal doses (570 mW/cm^2) Tc was crossed and loss in cellular viability was evident. In conclusion, nanoplatelets behave as logic gates having temperature and magnetic field as inputs and as the output a Yes/No answer to the question "was the 42 ºC barrier crossed?". This proof-of-concept opens the pathway to other noteworthy applications such as monitoring temperature thresholds in heat-triggered release of drugs/genetic therapy and in ultrafast polymerase chain reactions

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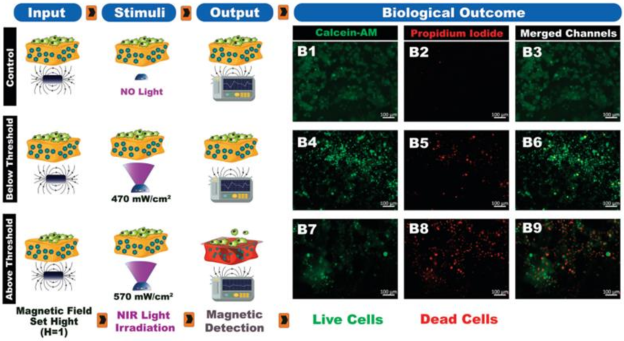

Figure 1: Reprinted from Oliveira-Silva, R. *et al*. Mater. Horiz., 2019, Advance Article

Enhancement of local Spin-Orbit Coupling effects in TMDC's/graphene heterostructures mediated by disorder

Armando Pezo, Jose H. Garcia, Adalberto Fazzio, Stephan Roche

Autonomous University of Barcelona,
Edifici ICN2 Campus de la UAB,
Av. de Serragalliners, s/n, 08193 Bellaterra,
Barcelona, Spain
armando.pezo@icn2.cat

In recent years, there is considerable interest in understanding the electronic and transport properties of graphene-based heterostructures. In particular, the heterostructure formed by graphene and two-dimensional transition metal dichalcogenides(TMDC’s) is currently under extensive research [1] due to recent measurements of the Spin Hall Effect [2], and the discovery of a giant spin lifetime anisotropy [3]. However, the effects of disorder in these heterostructures is still lacking, mostly due to the high dimensionality of the systems arising from the two incommensurate lattices conforming it. In this work, we use the very recent implementation of the spin-orbit coupling of the SIESTA package [4] deployed in a high-performance computing environment, for showing the effect of disorder in the spin-texture of graphene/TMDC’s heterostructures. As our main result, we found that localized defects produced a local modification of the spin-orbit coupling which can be used to increase and tune spin-orbit related phenomena as the spin Hall effect.

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Figures

Figure 1: Bilayer supercell for TMDC/graphene heterostructure.

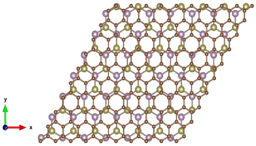
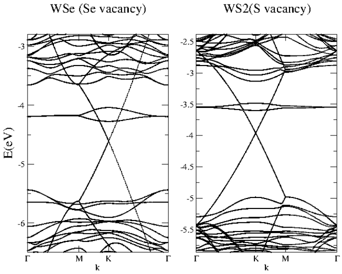


Figure 2: Electronic Band structure for WSe2 and WS2 with a vacancy in the TMDC.



Interactions between conducting additives and redox couples dispersed in flow cell electrolytes

E. Pujades-Otero, D. Tonti, N. Casañ-Pastor

Institut de Ciència de Materials de Barcelona (ICMAB, CSIC)
Campus UAB, E-08193, Bellaterra, Barcelona, Spain
epujades@icmab.es

The use of nanocarbons as dispersed conducting additives can bring interesting advantages in the electrolyte of electrochemical storage devices as this material can ensure a high conductivity and area. Moreover, the introduction of multiredox nanosized oxides (redox couples) dispersed in the electrolyte can also lead to remarkable improvements, as seen in Li/air batteries [1,2]. These oxides can act both as redox mediators and catalysts for the oxygen reduction or evolution reactions (ORR, OER) that take place during the battery cycling. Polyoxometalate clusters or other nanoparticles such as FeOx and IrOx are already known by their catalytic activity in O_2 reduction and reoxidation processes [3].

Herein, the influence of different types of carbon and multiredox nanosized oxides in aqueous alkaline and organic media has been studied for Zn/O_2 flow cell electrolytes. Graphene, graphene oxide, carbon black and carbon nanotubes have been used as conducting additives whereas polyoxometalates and IrOx have been used as multiredox nanosized oxides. Furthermore, hybrids between carbons and the nanosized oxides have also been tested, as a significantly enhanced catalytic activity is expected being the oxides coupled to the carbons. In several cases we do observe a synergy between the redox and the conducting species giving rise to enhanced currents and lower overpotentials. The relevant parameters and hypothesis for a mechanism will be discussed.

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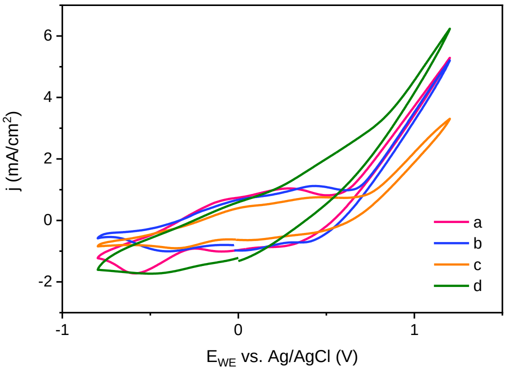

Figure 1: Cyclic voltammetries at 50 mV/s of OER and ORR on IrOx electrodes in a) K_2CO_3 0.1 M (aq) and with addition of b) IrOx solution, c) carbon nanotubes and d) IrOx and carbon nanotubes.
As observed in figure 1, the addition of both carbon nanotubes and IrOx in an aqueous alkaline media results in a synergy that leads in a more favorable OER, whereas no large effect compared to the blank is seen when only adding neither carbon nanotubes nor IrOx.

Tunable Circular Dichroism and Valley Polarization in the Modified Haldane Model

Marc Vila,[1,2] Nguyen Tuan Hung,[3] Stephan Roche,[1,4] Riichiro Saito[3]

1 - Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain.
2 - Department of Physics, Universitat Autònoma de Barcelona, Campus UAB, Bellaterra, 08193 Barcelona, Spain.
3 - Department of Physics, Tohoku University, Sendai 980-8578, Japan.
4 - ICREA - Institució Catalana de Recerca i Estudis Avancats, 08010 Barcelona, Spain.

marc.vila@icn2.cat

Circularly polarized light is at the core of many different and intriguing properties such as circular dichroism [absorption is different between left- and right-handed circularly polarized light (σ_+ and σ_-)] and valley polarization (σ_+ and σ_- are absorbed at a specific valley K/K' in a hexagonal two-dimensional material). In this presentation, I will discuss the optical properties of a recently proposed modification of the Haldane model [1]. We study the polarization dependence of optical absorption for the modified Haldane model, which exhibits protected antichiral edge modes in presence of sample boundaries and is argued to be realizable in Weyl semimetals or in graphene with induced spin-orbit coupling and magnetism [2].
A rich optical phase diagram (Figure 1) is unveiled, in which the correlations between perfect circular dichroism, pseudospin and valley polarization can be tuned independently upon varying the Fermi energy. Importantly, perfect circular dichroism and valley polarization are achieved simultaneously, a feature not yet observed in known optical materials. This unprecedented combination of optical properties suggests some interesting novel photonic device functionality (e.g. light polarizer) which could be combined with valleytronics applications (e.g. generation of valley currents).

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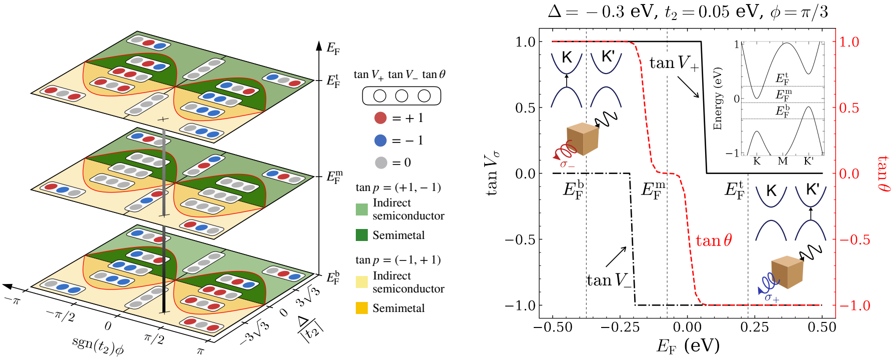

Figure 1: (Left) Optical phase diagram of the modified Haldane model [2]. Circular dichroism, valley polarization and pseudospin polarization is represented by the values $\tan\theta$, $\tan V_\sigma$ and $\tan p$, respectively. **(Right)** Tunability of circular dichroism and valley polarization with varying Fermi energy.

Posters Flash

Design of chemotactic nano-motors based on enzyme catalysis

Azzurra Apriceno[a], Lorena Ruiz-Pérez[ab], Cesare De Pace[a], Giuseppe Battaglia[ab]

[a]Department of Chemistry, University College London, , 20 Gordon Street, Kings Cross, London, UK
[b] The EPSRC/Jeol Centre for Liquid-Phase Electron Microscopy at UCL
a.apriceno@ucl.ac.uk

The movement of organisms in response to stimuli of different nature is a well-established phenomenon in nature. Bacteria, sperm cells and uni- or multicellular organisms are able to adapt themselves to environmental changes and translate by sensing external signals and adapting their motion towards or away from the sensed signals.[1] The stimuli, and the consequent generated motion that organisms experience, can be related to variations in the temperature (thermotaxis), magnetic field (magnetotaxis), adhesion forces (haptotaxis), and chemical gradient (chemotaxis).

The migration of cells towards chemical sources is a fundamental phenomena for many biological processes such as immune defense, wound healing and cancer metastasis.[2] Chemotaxis of cancer cells is thought to promote cancer metastasis, for example melanoma cells are directed out from tumors towards higher levels of a chemoattractant- lysophosphatidic acid in order for the cells to intravasate into local blood vessels.[3] However, the role of chemotaxis in the mechanisms of cellular vesicular transport is still relatively unexplored and poorly understood. Vesicular transport plays a central role in the traffic of molecules between different membrane-enclosed compartments rending it a major cellular activity.[4]

The main purpose of the present study is to explore the role of chemotaxis on vesicles transport and, particularly, elucidate the mechanisms of particles migration. Lipid nano-vesicles (liposomes) have been chosen as simple model vesicles with the aim of mimicking and reproducing the biological compartments that are involved in these cellular processes. The encapsulation and confinement of catalytically active biomolecules e.g. enzymes, within liposomes allows to investigate the liposomes response to various concentration gradients of specific substrates under a *self-diffusiophoretic* regime. To this aim, a film rehydration approach has been carried out in order to encapsulate glucose oxidase within 100 nm phosphatidylcholine-based liposomes. The motion experienced by empty and enzyme-encapsulated liposomes in presence of chemical gradients has been investigated by tracking and analysing singular particles trajectories over time and space.

Understanding the behaviour of the modelled system will significantly improve the design of self-propelling nano-devices with the ability of performing challenging tasks such as selective transport and site targeting within cellular environment.

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Dynamic equilibrium in CTAB gold nanoparticle bilayer, and the consequent impact on the exposure to biological fluids and on the formation of the nanoparticle protein corona.

F. Barbero†‡, O. Moriones†‡, N.G. Bastús†, V. Puntes†‡§‖
† Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain
‡ Universitat Autònoma de Barcelona (UAB), Campus UAB, 08193, Bellaterra, Barcelona, Spain
§ Vall d'Hebron Institut de Recerca (VHIR), 08035, Barcelona, Spain
‖ Institució Catalana de Recerca i Estudis Avançats (ICREA), P. Lluís Companys 23, 08010 Barcelona, Spain
francesco.barbero@icn2.cat

Gold nanoparticles in solution are usually surrounded by stabilising molecules that avoid aggregation and determine their surface properties, highly influencing their behaviour. Study the surfaces natures is of paramount importance in the development of nanoparticles applications. A widely used stabilizer is the cationic surfactant CTAB, mainly because allowed the controlled synthesis of several shapes of gold nanoparticles, moreover the resultant particles are commonly used as cationic model in nano-safety studies. The physicochemical properties of the evidenced CTAB bilayer coating the surface of the particles has been largely investigated, but not its static vs dynamic nature. The present work was aimed to shed light on this question and to understand its impact on nanoparticles evolution in biological and environmental scenarios. A systematic physicochemical study of CTAB bilayer of gold nanospheres and nanorods was carried out, exploring the role of the surfactant in excess in solution on the nanoparticles surface properties and colloidal stability. The results highlighted the presence of a dynamic equilibrium between the CTAB present in the bilayer and the free surfactant in solution, resultant in the existence of multiple natures of the surfactant bilayer depending on the whole CTAB concentration. The dynamicity of the bilayer entail that this dispersions always contain free CTAB, was underlined that cannot be prepared a colloidally stable sample that present in the bilayer a concentration of surfactant higher than the free one. The impact of the dynamic equilibrium on the particle exposition to biological fluids and on the formation of nanoparticles protein corona was also studied, highlighting a different nanoparticles behaviours depending on their purification grade. During this work a simple and low-cost gold nanoparticle phase transfer strategy from water to organic solvents was also developed.

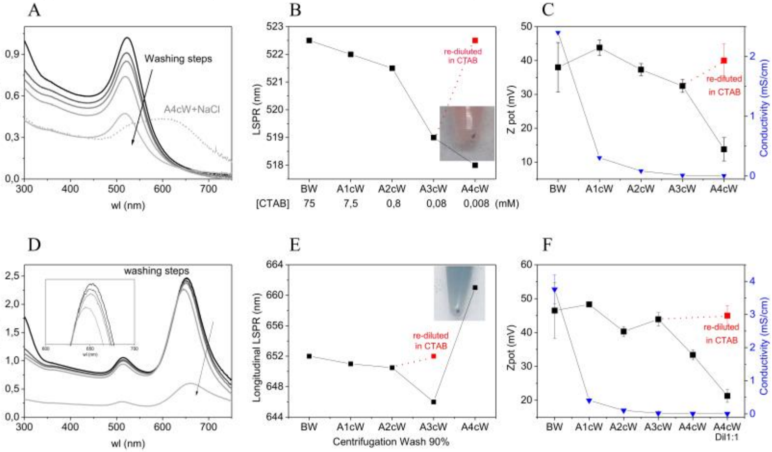

Figure 1: LSPR, ζ potential and colloidal stability changes observed along NPs centrifugation washing steps. (A, D) UV-Vis spectra of AuNS and AuRod after several purification by centrifugation steps, in each stage 90% of the supernatant volume was removed and the samples were filled with an equal volume of water.(B-E) LSPR value of AuNPs after each purification step; the photos represent the samples after 4 washing steps and is possible to notice that the NP pellets were not totally re-dispersable. (C, F) ζ potential (■) and conductivity (▼) of AuNPs after each purification step.

Nanostructuration in insulating $La_2Ni_{1-x}Mn_{1+x}O_6$

M. Bernal-Salamanca[1]**,** Z. Konstantinović[2], Ll. Balcells[1], C. Frontera[1], V. Fuentes[1], E. Pannunzio-Miner[3]
S. Valencia[4], A. Pomar[1], B. Martínez[1]

[1]Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus UAB, 08193 Bellaterra, Spain.
[2]Institute of Physics Belgrade (CSSPNM), University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia.
[3]CICTERRA-Fac. de Ciencias Exactas, Físicas y Naturales, Av. Velez Sarfield 1611, Ciudad Universitaria, Cordoba, Argentina
[4]Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str.15, 12489 Berlin, Germany.

mbernal@icmab.es

The tendency of some functional perovskite oxides toward self-organized growth and spontaneous nanostructuration, offers enormous potential for the implementation of new nanodevices. Among them, double perovskite La_2NiMnO_6 is one of few ferromagnertic materials with semiconducting character [1]. In this work, we report the epitaxial growth of non-stochiometric $La_2Ni_{1-x}Mn_{1+x}O_6$ thin films on $SrTiO_3$ (001) substrates by RF magnetron sputtering using a stoichiometric ceramic La_2NiMnO_6 target prepared by sol-gel method. Structural and magnetic properties of non-stoichiometric $La_2Ni_{0.4}Mn_{1.6}O_6$ thin films, prepared at high temperature (T= 800-900 °C) and low oxygen pressure (P_{O2}=130-150 mTorr), are studied as a function of annealing conditions (Fig.1). Irrespective to the growth conditions used, films grow fully strained showing insulating behavior. While Atomic Force Microscopy (AFM) show flat surfaces with low roughness, Scanning Electron Microscopy (SEM) images indicate the presence of ramified clusters, randomly and uniformely distributed throughout the surface, associated to low adatom mobility during film growth, as typically observed in metal depositions (Fig.1(a)). High temperature annealing treatment after film growth, as typicaly used to improve magnetic properties, promotes closening of ramified clusters and the appearance of monolayer vacancy islands (Fig.1(b)). Increasing annealing temperature up to 900 °C, ramified clusters disappear completely leaving only round vacancy islands (Fig.1(c)). In addition, the spontaneous formation of nanometric cubes can be observed inside of vacancy islands, probably related with the formation of nickel oxide clusters previously reported in [2]. X-ray absorption spectroscopy (XAS) experiments reveal that these formations in the films are likely due to Mn^{2+} inclusions on the surface.

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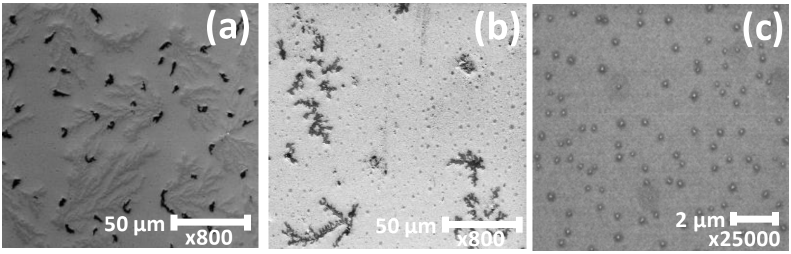

Figure 1: SEM images of LNMO thin films grown on STO (001) substrate under low oxygen pressures (P_{O2}=140 mTorr) at high temperature (a) without annealing process and with different annealing under 420 Torr O_2 (b) at 850°C and (c) at 900°C.

Enhancement of thermal properties of graphene-based nanofluids

E Chavez-Angel[1], M.R. Rodirguez-Laguna[1,2], P. Gomez[1], C.M. Sotomayor Torres[1,3]

[1] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology (BIST), Campus UAB, Bellaterra, 08193 Barcelona, Spain.
[2]Dept. Chemistry, Universitat Àutonoma de Barcelona, Campus UAB, Bellaterra, 08193 Barcelona, Spain
[3]ICREA- Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain.

emigdio.chavez@icn2.cat

Conventional liquids such as: water, ethylene glycol, and mixtures of these two are popular and are widely used as coolants for many electronic devices.[1] But, a major problem of these coolants is the low thermal conductivity (0.2-0.6 $WK^{-1}m^{-1}$), which is too small to meet the coming needs and challenges in the field. One way to overcome this barrier is by using solid particles dispersed in fluids to improve their thermal properties.[2,3] The dispersion of nanomaterials is an effective means to enhance the thermal properties of fluids, however, the mechanism behind has not yet been established. In this work, we have developed highly stable surfactant-free graphene nanofluids with enhanced thermal properties based in DMAc, DMF and NMP; and determined the influence of graphene concentration on the thermal conductivity, specific heat capacity, sound velocity and Raman spectra. Results show maximum enhancements of 48% and 18% for the thermal conductivity and specific heat capacity, respectively. The displacement of several Raman bands as a function of graphene concentration in DMAc and DMF suggests that the solvent molecules are able to interact with graphene surfaces strongly indicating a possible local π-π stacking. These interactions together with the naturally formed hydrogen bonds between DMAc and DMF molecules create a dynamic order, in which graphene acts as an “accelerating centre” for thermal waves. As far as we are aware this is the first time that a mechanism behind k enhancement in NFs is proposed and supported by both experimental and theoretical simulations. Our study provides considerable insight into the field of thermal transport in dynamic systems, as liquids and NFs, addressing a fundamental problem in NFs. DFT and MD methods were applied to shed light on the spectroscopic results. The calculations showed that the most frequent DMF orientation with respect to graphene was the parallel one. We found that three parallel configurations presented the highest occurrence. Later, these configurations were used as an input for DFT simulations. It showed that these configurations were the most energetically favourable, facilitating π-π stacking. For the Case of NMP, we did not find any significant modification on the thermal properties and/or in the Raman spectra. Suggesting that the enhancement of thermal conductivity for these fluids is strongly correlated with the displacement of these Raman modes.

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Unlabelled Confocal Microscopy Imaging of 15 to 150 nm Gold Nanoparticles

Muriel F. Gusta[1], Neus G. Bastus[2], Victor F. Puntes[1,2,3]

1. Vall d'Hebron Institut de Recerca, Pg de la Vall d'Hebron 119-129, 08035 Barcelona, Spain
2. Institut Catala de Nanociencia i Nanotecnologia, Campus de la UAB, 08193 Barcelona, Spain
3. Institut Catala de Recerca i d'Estudis Avançats, Pg Lluís Companys 23, 08010 Barcelona, Spain
muriel.freixanet@vhir.org

Noble metal nanoparticles (NPs), particularly gold (Au) and silver (Ag) NPs, have recognized relevance in chemistry, physics, and biology because of their outstanding optical, electrical, and photothermal properties. Optical properties, as UV-vis spectra and localized surface plasmon resonance, are easily measurable signatures indicative of their morphology (size and shape), composition, surface chemistry, aggregation state and physical environment that can be used to identify molecular targets and chemical transformation processes.1 Due to the growing interest in the use of metal NPs in medicine and biology, detailed cellular studies are required before their application in vivo for treatment or diagnostic purposes.2 Herein, we present the observation of unlabelled Au NPs on Confocal Laser Scanning Microscopy (CLSM), by using the light reflectance instead of the commonly used fluorescence mode. The NPs size resolution limits for CLSM observation is studied experimentally. Theoretical calculations, of the size-dependent optical properties are also presented to support this argument. The Au NPs used were synthesized using the seeded growth citrate reduction method3, and the NPs sizes range from 15nm to 150nm. Full characterization of the produced NPs was also performed by Transmission Electron Microscopy (TEM), UV-Vis spectroscopy and Dynamic Light Scattering (DLS). Further, the intracellular observation of different sizes of Au NPs using the reflectance mode is also presented. This work reveals as a method to observe NPs in living systems in real-time and non-invasive way, which can be extended to other inorganic NPs.

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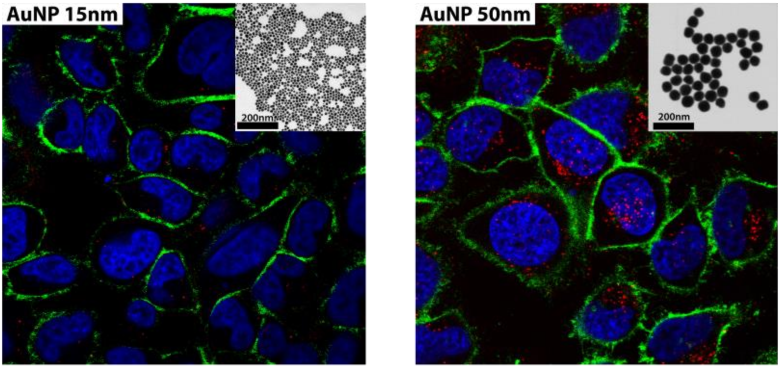

Figure 1: Confocal Imaging of Au NPs, 15nm (left) and 50nm (right), on *in vivo* HeLa cells

Fabrication of Reduced Graphene Oxide Supercapacitor Electrodes Through Easily-scalable Laser-method

Pablo García Lebière[1], Nil Posa i Campanyà[1], Angel Pérez del Pino[1], Enikö György[1,2]

1 Instituto de Ciencia de Materiales de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain
2 National Institute for Lasers, Plasma and Radiation Physics, P. O. Box MG 36, 77125 Bucharest, Romania.
pgarcia2@icmab.es

The outstanding properties of graphene based materials have focused great interest in the recent years. Their high intrinsic electric conductance, high specific surface area, good flexibility, fast charge-discharge rate, cycling stability and long lifetime make these materials suitable for energy storage applications, for instance, in supercapacitor devices [1-3].

An easily-scalable to industry laser-method for the reduction of graphene oxide (GO) and production of surface layers consisting of graphene-like materials is presented. A highly insulating GO layer is deposited by drop-casting onto flexible substrates and is irradiated with visible laser radiation, in order to induce its chemical reduction, leading to the formation of conducting graphene-like compounds [4]. The developed laser-based method has many advantages including fast prototyping and high throughput due to the reduced number of technical steps, environmental friendliness, and high precision [5]. This technique also allows for the compositional modification of the initial layers constituted by various compounds. Particularly, the laser irradiation of GO and transition metal oxide (TMO) precursors, TMO acetates, provokes the crystallization of TMO nanostructures on the reduced graphene oxide (rGO) sheets' surface, adding pseudocapacitance to the capacitive rGO structure [6]. The resulting rGO-TMO layers show improved supercapacitive energy storage performances, investigated by means of different electrochemical techniques.

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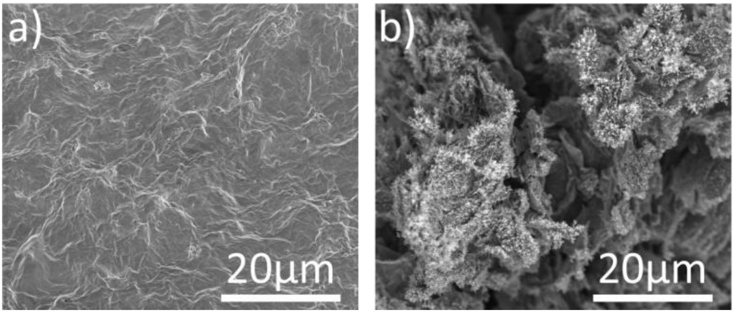

Figure 1: GO as-deposited (a) and after laser-method reduction (b).

pH-responsive NanoImmunoTherapy for Rheumatoid Arthritis

Virgínia Moura Gouveia, Loris Rizzello, Claudia Nunes, António Oliveira, Salette Reis, Giuseppe Battaglia

Department of Chemistry, University College London, 20 Gordon Street, Kings Cross, London WC1H 0AJ, United Kingdom
virginia.mgouveia@gmail.com

Rheumatoid arthritis (RA) is a chronic systemic inflammatory autoimmune disease characterized by progressive synovial inflammation [1]. Current therapies include glucocorticoid and disease-modifying anti-rheumatic drugs [1]. Despite well-known immunosuppressive and anti-inflammatory activity, these drugs are associated with deleterious side effects. Mostly due to the limited selectivity, rapid clearance and widespread biodistribution into non-target tissues [1]. Macrophages and synoviocytes found within the synovium are responsible for the modulation of the synovial inflammatory response [1]. In this study, we present pH-responsive polymersomes made of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) and poly(2-(diisopropylamino)ethyl methacrylate) (PDPA) diblock copolymer as suitable drug delivery nanocarriers able to target and effectively mediate the intracellular drug release along the endocytic pathway [2-3]. The cell selectivity is ascribed to the high targeting specificity of PMPC block to the scavenger receptor B type I [2-3]. Once inside the synovial cell, the PDPA block bestows the necessary pH trigger hence enabling drug's endosomal escape [2-3].

Polymersomes were characterized in terms of vesicle size, morphology and drug loading capacity. Additionally, drug release studies mimicking blood (pH 7.4), inflamed synovium (pH 6.5) and endosomes (pH 5.0) physiologic microenvironments were performed to evaluate polymersomes stability and pH responsiveness. The *in vitro* performance of drug loaded polymersomes in human macrophages and synoviocytes included live cell uptake kinetics and anti-inflammatory efficacy related to nuclear factor kappa B signaling transduction using confocal laser scanning microscopy. Additional cells response to the anti-inflammatory activity of drug loaded pH-responsive polymersomes was assessed by quantitative polymerase chain reaction and enzyme-linked immunosorbent assay. This approach takes advantage of the pH sensitivity, the selectivity and stability of pH-responsive polymersomes in order to increase the bioavailability of drug within target synovial cells. To this end, polymersomes have the therapeutic potential to enhance the drugs anti-inflammatory and immunosuppressive efficacy, while limiting well-known off-target side effects in chronic RA therapy.

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Precise featuring the size, surface charge and dye loading of highly monodisperse silica nanoparticles for developing ¨stealth¨ charged vehicles for nanomedicine

Oscar H. Moriones [a, b], Neus G. Bastús [a], and Victor Puntes [a, b, c, d]

[a] Institut Català de Nanociència y Nanotecnologia (ICN2),Campus UAB,08193. [b] Universitat Autonòma de Barcelona (UAB), campus UAB, 08193.[c] Vall d`Hebron Institut de Recerca (VHIR), 08035.[d] Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010, Barcelona, Spain.

oscarhernando.moriones@icn2.cat

Chemical modification of silica particles leads to a variety of applications in biomedical fields, such as, drug delivery, gene therapy and molecular imaging. In this work, sequential modification of size, surface charge, dye loading and colloidal stability in physiological media of monodisperse silica nanopartciles by one-pot adapted Stöber[1] method is described. The radius of the silica cores with narrow sizes distributions SD≥10% can be systematically controlled in the range of 20 to 300 nm by the water/TEOS ratio in the starting reaction. The surface charge modification were done by covalently functionalization the negavite surface hydroxyl groups with the (3-aminopropyl)trimethoxysilane (APTES), considered to induce a positive surface charge by siloxane bonds to the silica surface and exposing amine ends. Our results allowed systematically controll the surface charge from -42.0 mV to 45.0 mV and tunning the isoelectric point (IEP) from 5.7 to 8.6. In addition, the degree of amine grafting on the passivated surface was determined by the ninhydrin assay. The primary or secondary amines attached on the surface, reacted with nynhydrine, yielding a bright purple complex known as Ruhemann´s purple. The numbers of amine molecules per surface grafted obtained were 1.50 to 4.43 NH_2 molecules/nm^2. The fluorescent molecules were incorporated during the particle formation by imposition of the dye on the silica network via the formation of a covalent bond between the dye and a silane coupling agent (APTES). Dyes having an isothiocyanate functional group were incorporated following a thiourea-linkage and the ones having succinimidyl esters followed a carboxamide-linkage. The colloidal stability in physiological media was also evaluated, in order to improve systemic circulation time and shield the nanoparticle surface from aggregation, opzonization and phagocytosis. A coating-step strategy using an inert polymer the mPEG5K silane were done in order to confer steric stabilization, surface charge protection and resistance for the interactions with components of the blood stream, imparting “stealth” properties.

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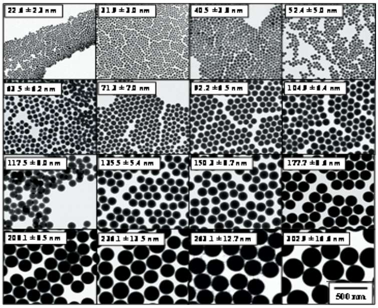

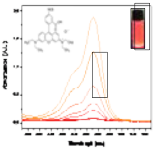

Figure 1: (A) Transmission electron microsco
synthesis of silica nanoparticles. Particle siz
spectra of the 50nm silica nanoparticles
Rhodamine B isothiocyanate (RBITC), Tetra
(AF350NHS). Different Rainbow-like nanop
precursors during the one-pot modified Stöbe

Hollow PdAg/CeO_2 heterodimer nanocrystals as structured catalyst for the selective hydrogenation of alkynes

Javier Patarroyo, [a] Jorge A. Delgado, [b] Florind Merkoçi, [a] Aziz Genç, [a,c] Jordi Arbiol, [a,e] Neus G. Bastus, [a] Cyril Godard, [d] Carmen Claver [b,d] and Victor Puntes [a,e,f]

[a.] *Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain.* [b]*Centre Tecnologic de la Química, C/Marceli Domingo, 43007 Tarragona, Spain.* [c]*Department of Metallurgy and Materials Engineering, Faculty of Engineering, Bartin University, 74100, Bartin, Turkey.* [d]*Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, C/Marceli Domingo 1, 43007 Tarragona, Spain.*[e]*ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Catalonia, Spain.*[f] *Vall d'Hebron Institut de Recerca (VHIR), 08035, Barcelona, Spain*

javier.patarroyo@icn2.cat

In the present work, we report a facile synthesis of a new class of heterodimer nanocrystals (NCs) with alloyed hollow morphologies (PdAg/CeO_2) via the galvanic replacement reaction between Ag/CeO_2 NCs used as sacrificial templates and K_2PdCl_6 used as Pd precursor, these heterodimer NCs were tested as catalysts for the selective hydrogenation of alkynes.

These new nanostructures combine the beneficial effect of alloying Pd with Ag in a single NC hollow domain with the formation of active sites at the interface with the CeO_2 counterpart. The PdAg/CeO_2 NCs display well to excellent alkene selectivity for aliphatic alkynes. For the specific case of hydrogenation of internal alkynes such as 4-octyne, very low over-hydrogenation and isomerization products were observed over a full conversion regime, even after prolonged reaction times. These catalytic properties were remarkably superior in comparison to commercial Pd-based monometallic catalysts and similar or superior to industrial standards, such as the Lindlar catalyst. These effects were attributed to firstly, the promotional effect of Ag on the moderation of the reactivity of the Pd phase, and secondly, a synergic effect between the CeO_2 NCs and the hollow bimetallic alloy at their interface.

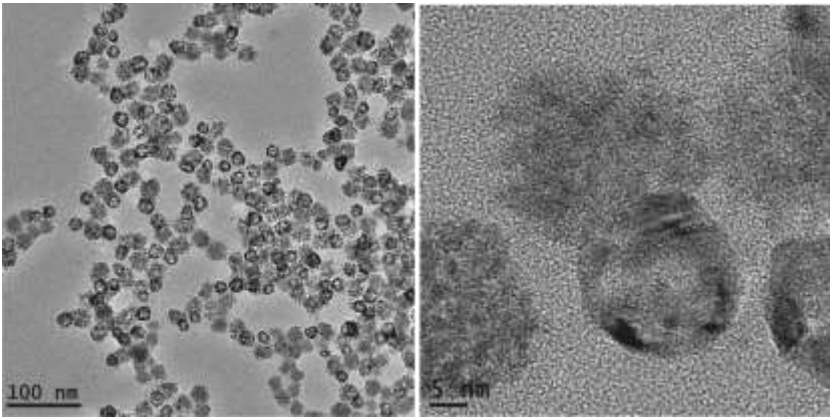

Figure 1: TEM images of PdAg/CeO_2 heterodimer nanocrystals

Traking nanomotors for in vivo applications using nuclear imaging techniques

Cristina Simó[a], Tania Patiño[b], Ana Hortelano[b], Unai Cossío[a], Vanessa Gómez-Vallejo[a], Jordi LLop[a], Samuel Sánchez[b,c]

[a]CIC BiomaGUNE, Paseo Miramón 182, 20014 San Sebastián, Guipúzcoa, Spain
[b]Institute for Bioengineering of Catalonia (IBEC), Baldiri Reixac 10-12, 08028 Barcelona, Spain
[c]Institució Catalana de Recerca i Estudis Avançats (ICREA), Passeig de Lluís Companys, 23, 08010 Barcelona, Spain
csimo@cicbiomagune.es

Micro/nanomotors, which are micro/nanoscale devices capable to induce self-propulsion in fluid environments, have recently gained attention for different biomedical applications [1,2]. Initial works reported in the literature described micro/nanomotors able to swim in non-biocompatible matrixes such as aqueous hydrogen peroxide. Moving towards *in vivo* applications, enzyme catalysis has emerged as a biocompatible and powerful alternative to produce self-propulsion. However, tracking these micro- and nano-devices *in vivo* and at the whole body level still remains a challenge. Here, we describe the application of radiollabelling followed by Positron Emission Tomography (PET) imaging to achieve the time-resolved tracking of urease-functionalized nanomotors as potential drug delivery agents for bladder cancer.

Fully mesoporous silica nanoparticles (MSNP) with a mean diameter of 480 nm were fabricated and modified with amine groups using previously reported methods [3]. The MSNP were then functionalized with urease and heterobifunctional H_2N-PEG-SH via glutaraldehyde crosslinking, to obtain pegylated urease-powered nanomotors. The available thiol groups were then used for anchoring 20 nm gold nanoparticles. The efficient radio-fluorination of the nanomotors was achieved by the reaction (pH = 8, room temperature, 35 min) between the amine groups of the urease and 6-[^{18}F]fluoronicotinyl-2,3,5,6-tetrafluorophenyl ester ([^{18}F]FPy-TFP), which was prepared following a previously reported procedure [4].

PET Imaging studies in a labyrinth-type phantom (Fig. 1a) clearly showed the self-propelling capacity of the nanomotors in the presence of urea (Fig. 1c) while no significant movement was observed in pure water (Fig. 1b). In vivo biodistribution studies in rodents after intravenous administration showed accumulation of the nanomotors in lungs and liver, majoritarily. Our results clearly demonstrate the suitability of our approach for the *in vivo* tracking of nanomotors.

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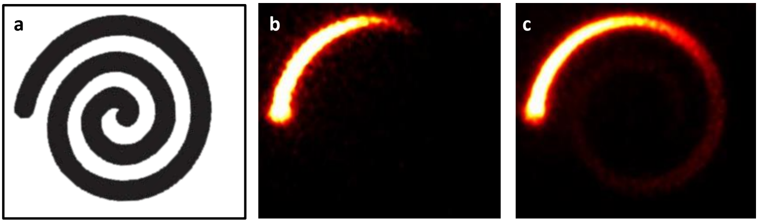

Figure 1: (a) Schematic top view of the laberynth-type phantom; (b) Image obtained at t=60 min after seeding of nanomotors in water; (c) Image obtained at t=60 min after seeding of nanomotors in 300 mM aqueous urea solution.

Epitaxial Thin Films of La_2CoMnO_6 and La_2NiMnO_6 Ordered Double Perovskites by Polymer Assisted Deposition

Hailin Wang[1], J. Gazquez[1], C. Frontera[1], M.F. Chisholm[2], A. Pomar[1], B. Martínez[1], N. Mestres[1]

[1] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, Barcelona, Spain

[2] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, USA

hwang@icmab.es

Abstract

Epitaxial double perovskite La_2CoMnO_6 (LCMO) and La_2NiMnO_6 (LNMO) thin films are highly attractive due to their ferromagnetic behavior and magnetodielectric effect near room temperature, making them promising materials for applications into new devices and spintronics.[1] However these properties are strongly dependent on the ordered arrangement of cations in the double perovskite $A_2BB'O_6$ structure.[2]

In this work, high quality epitaxial LCMO and LNMO films were grown on (001) $SrTiO_3$ substrates by a polymer assisted deposition (PAD) method.[3] In the PAD process, the different metal salt precursors were dissolved in an aqueous Polyethylenimine (PEI) polymer solution. This technique allows an easy control of stoichiometry by mixing different metal-polymer precursor solutions with the corresponding metal molar ratios. The precursor solutions were spin coated on (001)-STO substrates and the resultant coatings were thermally treated at 900 °C in flowing oxygen.

We show that the particular crystallization and growth process conditions of PAD (very slow rate, close to thermodynamic equilibrium conditions) promote high crystallinity and quality of the films, as well as B-site cationic ordering. The LCMO films show saturation magnetization values of about 6 μ_B/f.u. and a $T_c \approx 230K$, thus indicating full cationic ordering of Co^{2+}/Mn^{4+} in a double perovskite structure (fig. 1). Confirmation of of full Co/Mn cationic ordering is found by scanning transmission electron microscopy (STEM) measurements (fig. 2). The LNMO films show saturation magnetization values of about 4 μ_B/f.u. with $T_c \approx 260K$, indicating that the Ni^{2+}/Mn^{4+} cationic ordering needs to be improved.

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Figures

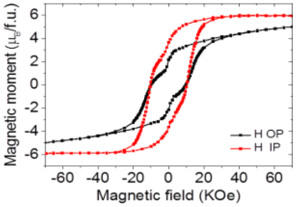

Figure 1: M-H loops recorded at 10K for a LCMO/STO film, displaying saturation magnetization value close to 6 μ_B/f.u. in good agreement with the theoretical value for fully ordered samples

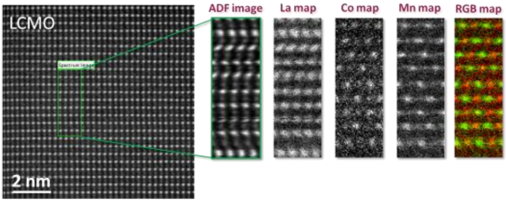

Figure 2: From left to right, Z-contrast image of the LCMO film, ADF image, atomic maps of La M, Co L, and Mn L absorption edges and RGB map produced by overlaying the Co (in red) and La (in green) elemental maps, indicating full cationic ordering

Posters

Preparation of organic modified Calcium Silicate Hydrates nanoparticles as additions for cement

Francisco Borja Aguirre[1], Edurne Erkizia[1], Juan José Gaitero[1], Jorge S. Dolado[2], Cyril Aymonier[3]

1.TECNALIA, División de Building Technologies, Parque Tecnológico de Bizkaia, Astondo bidea, 700 Edificio, 48160 Derio, Spain
2. Centro de Física de Materiales, Paseo Manuel de Lardizabal, 5 – E-20018 Donostia, Spain
3. CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
Francisco.aguirre@tecnalia.com

Abstract

Nanoadditions such as nanosilica [1] and certain calcium silicate hydrate nanoparticles can improve the fresh and hardened properties of cement paste. However, these materials tend to aggregate [2] and absorb high quantity of water when are added to cement mixtures reducing paste workability [3]. Because of that it is necessary to increase the aquous fraction in the mixture to improve the workability of pastes. However, increasing the water in cement matrix causes a reduction of its mechanical properties and reduces the beneficial effect we might obtain adding the nanoparticles. Traditionally superplasticizer admixtures are employed to reduce the water needed in cement mixtures, but they do not work well when nanoadditions are used [4].

The goal of this work is to improve the dispersion of the nanoparticles without having to add more water. This in mind, our study focuses on the synthesis and characterization of calcium silicate hydrate nanoparticles with organic functionalities obtained by subcritical hydrothermal reaction [5] and continuous supercritical reaction [6] that can be easily dispersed in cement suspensions [7]. In this work the synthesis of Xonotlite ($Ca_6Si_6O_{17}(OH)_2$) and Tobermorite ($Ca_5(OH)_2Si_6O_{16}\cdot 4H_2O$) with polyethylene glycol molecules will be discussed (see figure 1) [8]. Moreover, the rheological and mechanical performance of this nanoadditions during the early cement paste hydration will be shown.

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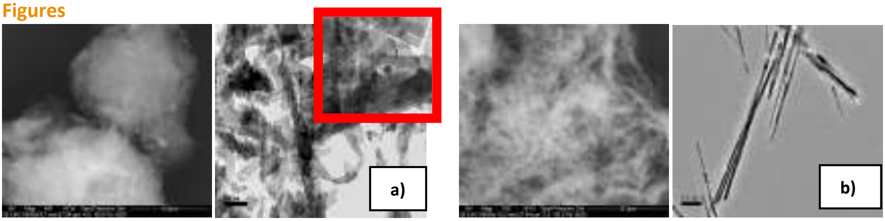

Figure 1: Transmission electron microscopy images of a) Tobermorite and b) Xonotlite synthesized by hydrothermal reaction and modified with PEG.

Vitamin C coated Gold sub-microparticles as a novel carrier to release stable Vitamin C inside the skin for topical application

María Elisa Alea Reyes, Marisabel Mourelle Mancini, Camila Folle, Gabriel Buendia Bordera*

Infinitec Activos S. L, Baldiri Reixac 15-21, Barcelona, Spain
*Instituto Láser de Fotomedicina en Teknon, Barcelona
mealea@infinitec.es

The antioxidant property of vitamin C is well-known for protecting cells from oxidative stress, but it can also induce collagen synthesis under a low intracellular concentration. In this study, we describe a rapid and efficient synthesis of gold sub-microparticles using ascorbic acid (AA) as reducing and stabilizing agent and GSH as a second ligand to compensate any H_2O_2 may be generate by AA oxidation under physiological conditions. The synthesized gold sub-microparticles were characterized by UV-visible, DLS, SEM and Z potential. Gold sub-microparticles display a spherical shape, low polydispersity and a size of 164 ± 24 nm. A stability study of Gold-submicroparticles was followed for 180 days, in water, glycerin and o/w emulsion at 40ºC. Results showed that Gold sub-microparticles is stable in all media up to 6 months. However, 50% of free AA is degraded in 1 and 2 days in water and Glycerin, and in o/w emulsion, the 50% of free AA is completelly degraded in 8 days. Skin penetration of Gold sub-microparticles was studied in pig-skin using Franz cells, concentrations were measured by HPLC after 20h. Results show that 74% of the applied dose was in the receptor fluid while 26 % remained inside the skin. Gold sub-microparticles skin permeability was 40 times higher than free AA or its salts (SAP and AG). Antioxidant activity of Gold sub-microparticles was evaluated by measuring free radical scavenging capacity determined by DPPH test. Gold sub-microparticles at 0,03% has the highest free radical scavenging efficiency from all products tested including AA and GSH at the same concentration. When AA is conjugated with both Gold and GSH, the antioxidant capacity was 66% higher than free AA and more than twice than free glutathione. A synergistic effect of both actives was observed when they were combined improving the neutralization of free radicals. Normal Human Dermal Fibroblasts (NHDF) cells were treated during 24 hours with AA, or Gold sub-microparticles at 0.003%. After the incubation, gene expression of COL1A1 was quantified by real-time PCR. Results showed that treatment with Gold sub-microparticles increased COL1A1 gene expression 66% more than free AA at the same concentration. Additionally, the efficacy of a cream containing Gold sub-microparticles (0.5%) vs cream containing 0.5% free AA was tested in vivo. Concentration of beta-carotenes in skin was assessed before and after 15 min continuos exposure to ozone or UV. Tests were performed in hemiface vs free AA. Gold submicroparticles application counteracted by 70% the beta-carotene loss induced by ozone or 50% by UV radiation. The protection observed with a free AA-containing cream was only 9%. Vitamine C Gold sub-microparticles containing GSH is more powerfull than free AA to protect from oxidative domage and to indice collagen synthesis in Skin cells.

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Supersonic acoustic waves in a supported layer

Francisco Céspedes, Francesc Alzina, **Jordi Gomis-Bresco,** Clivia.M. Sotomaor-Torres
Catalan Institute of Nanoscience and Nanotechnology (ICN2),
CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona,
jordi.gomis@icn2.cat

Rayleigh surface acoustic waves (RSAWs), the simplest of guided waves, can be described as non-dispersive surface acoustic waves (SAWs) propagating near the free surface of a homogenous medium with a finite penetration depth into bulk. Typically, in isotropic materials, the amplitude of RSAWs decays exponentially to zero within a depth of several wavelengths. The propagation of RSAWs in elastically anisotropic materials is more complex; thus, velocity and penetration depth strongly depend on the direction, plane of propagation, and elastic anisotropy ratio. Crystal surfaces also support pseudo-SAWs, the velocity of which exceeds the slow transverse bulk velocity. Pseudo-SAWs are leaky because of their coupling to the radiation continuum of bulk modes, but in isolated propagation directions the coupling to bulk modes disappears and true-RSAWs modes, termed supersonic surface waves (SSAWs) appear.[1] Guided waves can propagate in different geometries like supported layers (Sezawa or Rayleigh-Lamb-like waves). Similarly to crystal surfaces, supported layers present leaky waves when the phase velocity exceeds the slow transverse bulk velocity of the substrate.

In this work we present simulations based on the elastodynamic Green's function method to study the presence of SSAWs in supported layers. The effect of the crystallographic orientation of layer and substrate on the properties of the SSAWs is addressed.

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Figures

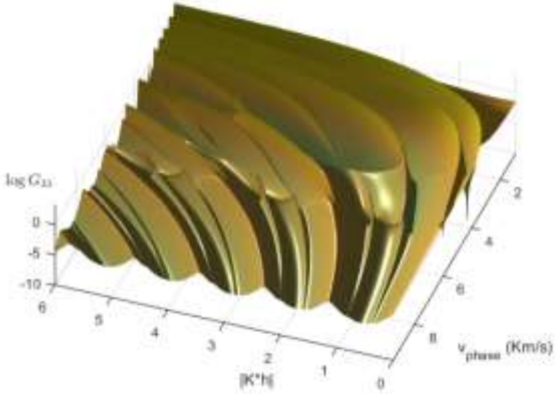

Figure 1: Map of the out of plane G33 component versus the phase velocity and the magnitude of the momentum for the phonon propagation on a h thick gold layer on top a (1 0 0) silicon substrate.

A Novel Class of Molecular Probes for Cellular Imaging

<u>De Pace, Cesare</u>[12]; Ruiz-Perez, Lorena[12]; Tian, Xiaohe[4]; Marchello, Gabriele[12]; Tian, Yupeng[4]; Battaglia, Giuseppe[123]

[1] Department of Chemistry, University College London, London, WC1H 0AJ, UK. [2]TheEPSRC/Jeol Centre of Liquid Electron Microscopy, University College London, London, WC1H 0AJ, UK. [3] Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology, Barcelona, 08028, Spain.[4] Department of Chemistry, Key Laboratory of Functional Inorganic Material Chemistry of Anhui Province, Anhui University, Hefei 230039, P. R. China.

c.pace@ucl.ac.uk

Nowadays, there are several probes to increase contrast in cellular imaging for confocal or electron microscopy. However, the majority of these probes often lack contrast for both microscopic technique or specificity for the target. Few probes display both microscopic techniques, yet they may hinder cell functions due to their size. Organometallic probes are engineered with nanoscopic design, specific targeting moieties to minimise the impact on cell function, and compatibility for light and electron microscopy. Organometals offer the outstanding advantage of owning high electron density due to their metal core. The metal core of the probe is usually made by elements which do not belong to cells. Thus, this peculiarity may offer the possibility to analyse the elemental composition of the specimen through energy-filtered transmission electron microscopy (EF-TEM) to further characterise the target of interest within the cell. Ir-Tub is a cyclometalated Iridium (III) complex, which intercalates between the subunit a and b of microtubulin, a critical component of the cell cytoskeleton. After treatment with Ir-Tub, microtubules in HepG2 cell were analysed by EF-TEM using a JEM2200 equipped with cold field emission gun (FEG) and W filter (figure 1). The binding site spacing of Ir-Tub, determined from the Ir chemical map, via the signal from the organometal is in very good agreement with the in silico model (figure 1c-e).[1] Organometallic probes are beginning to prove their unique properties as contrast providing agents for microscopic techniques such as confocal microscopy, TEM and EF-TEM, and liquid-phase TEM. Hence, compared to other labelling agents, organometallic compounds represent a new class of microscopic probes for investigating and understanding the mechanisms involved in cellular processes.

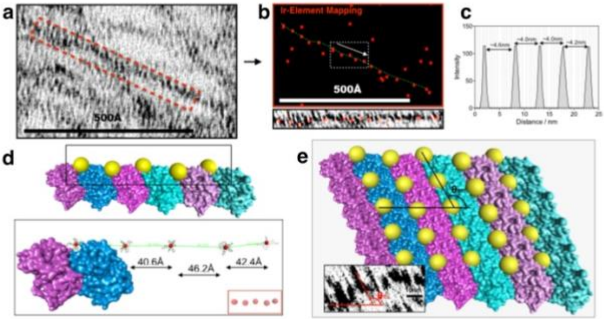

Figure 1. TEM evaluation of an organometallic probe (Ir-Tub) for microtubules on treated HepG2 cells. (a) Magnified image of a microtubule in the cell. (b) Iridium elemental map achieved in EF-TEM mode and (below) its superimposition with the TEM image, displaying how Ir-Tub complexes intercalate within microtubules stripes. (c) Distance measurement of neighboured Iridium elements, and (d) the comparison with the measured distance from the computational model. (d) Angle measurement of neighboured microtubules stripes with its horizontal line as polar coordinate system ($\theta_{tb}=68^{o}$), and similar measurement from polymerized microtubule model ($\theta_{md}= 68^{o}$).[1]

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Preparation and characterization of MnO_2/carbon nanowalls deposited on stainless steel substrate as electrodes for microbial fuel cells

Miguel Fernández Martín [1,2], Joan Martí-González [1,2] , Fernando Pantoja-Suárez [1,2,3], Islam Alshaikh [1,2],
Roger Amade [1,2], José Luis Andujar[1,2], Esther Pascual[1,2] and Enric Bertran-Serra[1,2]
[1] ENPHOCAMAT (FEMAN) Group, Dep. Applied Physics, Universitat de Barcelona, C/ Martí i Franquès, 1, 08028, Barcelona, España
[2] Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona
[3] Departamento de Materiales, Facultad de Ingeniería Mecánica, Escuela Politécnica Nacional, Ladrón de Guevara, E11 253, Quito, Ecuador, Address, City, Country
miguelfernandezmartin1@gmail.com

Abstract

Microbial fuel cells (MFCs) are bioelectrochemical systems that can produce bioelectricity from organic matter. Wastewater from urban, domestic or industrial origin can be used as a fuel to produce electricity. In addition, the amount of pollutants and contaminants decreases during the production of bioelectricity [1,2]. Thus, such bioelectrochemical systems produce renewable energy and, simultaneously, can be used as a novel technology for wastewater treatment. However, the efficiencies obtained are still too low and the output voltage of the MFCs need to be increased. In addition, the overall cost of the cell has to be reduced in order to promote this technology into the market. Here, we have studied the growth of graphene nanowalls on stainless-steel substrate 304 (SS), which can be used as electrodes in air-cathode MFCs. Growth parameters have been optimized to obtain vertically aligned and dense carbon nanostructures on both SS foil and mesh. MFCs with different electrodes have been prepared to study the effect of different parameters and to determine whether the presence of carbon nanostructures results in an increase of the electrochemical efficiency. An oxygen plasma treatment has been performed to study its effect on the properties of the electrodes. MnO_2 catalyst has been electrochemically deposited to catalyze the oxygen reduction reaction (ORR) that takes place on the cathode.

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Tuning the infrared absorption band of CuS nanoparticles for photothermal ablation applications

J.C. Ferrer, F. Rodríguez, J.L. Alonso, J. Capmany, S. Fernández de Ávila

Dpto. Ingeniería de Comunicaciones, Universidad Miguel Hernández, Av. Universidad, s/n, Ed. Innova, Elche, Spain
jc.ferrer@umh.es

Treatment of tumors by means of photothermal therapy using semiconductor nanoparticles is a promising alternative to chemotherapy or radiotherapy since the former technique may be limited to the target of interest and avoids the side effects of the later. Photothermal ablation is based on the heating of nanoparticles adhered to tumors by an infrared radiation for which the tissues are transparent. In order to become effective, nanoparticles should convert the optical power into heat efficiently.

Copper sulfides vary widely in composition with Cu:S ratios from 0.5 to 2 including numerous stable and metastable phases still to be fully characterized. Depending on the crystal structure, CuS_x nanoparticles may show an absorption band at the near infrared spectrum. In this work, a simple study of the influence of the Cu:S mole ratio on the activation of the IR absorption band is presented. Besides, the heating of a colloidal solution of CuS_x nanoparticles by means of a IR laser diode is demonstrated.

Five samples of CuS_x nanoparticles were synthesized by mixing 0.5M $CuCl_2$ and Na_2S solutions in a 4% polyvinyl alcohol (PVA) solution as stabilizer agent. The Cu:S mole ratio of the five samples were 1:2, 1:1.5, 1:1, 1.5:1 and 2:1. The resulting solutions were optically clear with colors ranging from copper brown to olive green. Transmission Electron Microscopy (not shown) observations were performed in order to confirm the presence of nanoparticles in the solutions.

Figure 1 shows the absorption spectra of the five samples. A common absorption band at lower wavelengths is observed independently of the proportion between Cu and S. However, the optical absorption around a wavelength of 874 nm depends on this variable. A minimal absorption is observed for the sample with a Cu:S mole ratio of 1:2. The absorption band increases for 1:1.5 ration and attains a maximum for Cu:S = 1:1. A further addition of copper results in a slight decrease of the absorption band.

In order to show the potential of the nanoparticles to be used in photothermal ablation applications, the solutions were illuminated by a 1 W infrared diode (λ = 860 nm) and the temperature variation was measured with a PT1000 temperature sensor during 25 minutes. Figure 2 shows the temperature increment of a bare PVA solution used as reference and the temperature variation of the samples with the highest (1:1) and lowest (1:2) absorption band. The higher temperature reached by the 1:1 solution is obviously related to the higher absorption of the infrared band which converts optical power into heat more efficiently.

Figures

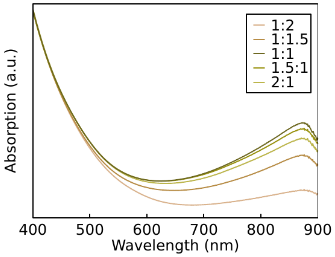

Figure 1: Optical absorption of CuS_x nanoparticle solutions with the Cu:S mole ratios shown in the inset.

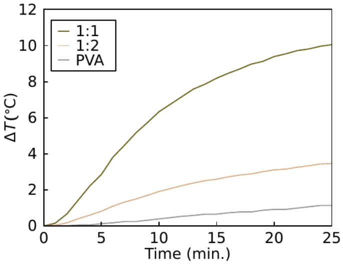

Figure 2: Temperature increment of the PVA reference solution and the samples with the highest (1:1) and lowest (1:2) IR absorption under ilumination of a λ = 860 nm laser diode.

Micro- and nanotexturization of Liquid Silicone Rubber (LSR) surfaces by injection moulding

N. Lozano-Hernández[1,2], G. Pérez[1], L. J. Del Valle[2], J. Puiggalí[2], E. Fontdecaba[1]

[1]Centre Tecnològic de Catalunya (EURECAT), Av. Universitat Autònoma, 23, Cerdanyola del Vallès, España
[2]Departament d'Enginyeria Química, Universitat Politècnica de Catalunya (UPC), c/ Eduard Maristany 10-14, Barcelona, España
nekane.lozano@eurecat.org

Micro and nanotexturization of polymeric surfaces can provide different promising functionalities and materials with potential applications in markets so different as the medical and automotive. Nature is a source of inspiration, a wide variety of surface with hierarchical structures at micro- and nanoscale can be found: lotus and taro leaves, gecko feet, butterfly wings or fish skin are some examples. These surface topographies possess wetting properties that are of commercial interest such as superhydrophobicity, self-cleaning, drag reduction or antireflection [1].

In the present work the material chosen is a Liquid Silicone Rubber (LSR): a two-component silicone (the base and the activator) with good elastic properties, extreme temperature resistance and low compression set. The replication of textures was carried out by the injection moulding process, due to his high productivity. The process starts with the fixation of the texturized film in the mould and its overmoulding. At the end, a texturized piece is obtained while the printed film remains on the mould. The parameters optimization of the injection moulding allows increasing the replication grade.

The LSR injection process consists in maintain the two-component mixture cold before pushing it on the heat mould, where temperature favours vulcanization. The use of polymeric texturized films obtained by nanoimprint lithography as an alternative to texturized moulds presents a heat insulating capability, which delays the silicone vulcanization and allows a complete filling of nanostructures [2]. Moreover, the low viscosity attained during processing of LSR (with respect other thermoplastic melts) makes it a good candidate for surface replication.

Therefore, Figure 1 shows a good replication grade of LSR surfaces with different geometries obtained during this work. Also, hydrophobic behaviour can be measured due to the change in the contact angle.

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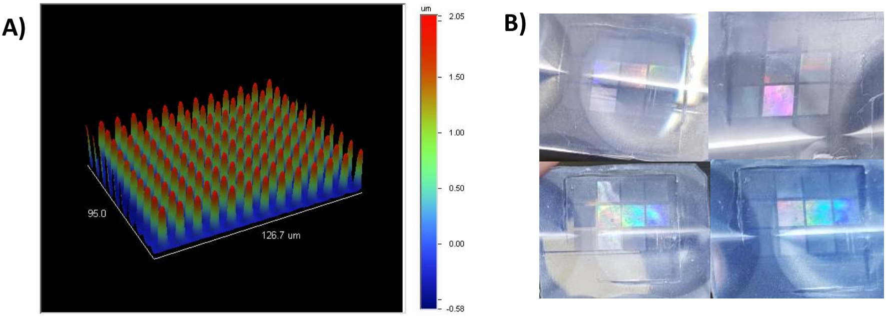

Figure 1: A) Interferometric microscopy images of LSR texturized surfaces: Pillars of 5 µm diameter and 2.5 µm height. B) Texturized surface of selected LSR pieces.

DFT insights into the electronic properties and adsorption of NO2 on metal-doped carbon nanotubes for gas sensing applications

Icell Sharafeldin , Nageh Allam

American University in Cairo (Egypt)
icell@aucegypt.edu

The gas sensing process involves complicated and precise adsorption mechanisms, and the selection of the right material is mainly based on “guess-and-check” procedures, which necessitates the search for a more systematic approach to discover optimum materials with required specifications. Herein, we report the use of ab initio first-principles methods to expedite the process of finding the material with the highest potential compared to in-lab trial and error. We focused on the NO2 adsorption mechanism of Cu-, Pt- and Ti-doped single-walled carbon nanotubes (SWCNTs). Modelling the isolated NO2 molecule indicated the formation of a band gap between the 3π* HOMO and 5σ* LUMO levels, which were found to be the electronic states primarily involved in the bonding process. Metal doping decreased the system stability and altered the SWCNT structure. NO2 exposure caused the transfer of electrons to the gas molecules, thereby enhancing the p-type conductivity of the M-SWCNT structure. The highest charge transfer to the NO2 molecule was observed for Ti-SWCNTs (0.456 eV), while the lowest was found for Cu-SWCNTs (0.351 eV). Ti-SWCNTs exhibited the highest stability and sensitivity as a potential NO2 gas sensing material out of the 3 investigated metal dopants

4D Imaging Techniques in Liquid Transmission Microscopy

Gabriele Marchello[1,2], Cesare De Pace[1,2], Neil Wilkinson[3], Lorena Ruiz-Perez[1,2], Giuseppe Battaglia[1,2]

[1]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[2]The EPSRC/Jeol Centre of Liquid Electron Microscopy at UCL, London WC1H 0AJ, UK
[3]Gatan UK, 25 Nuffield Way, Abingdon OX14 1RL, UK

Contact@ gabriele.marchello.16@ucl.ac.uk

Electron microscopy (EM) is a technique that exploits the interaction between electrons and matter to produce high resolution images down to atomic level. To avoid undesired scattering in the electron path, EM samples are conventionally imaged in solid state under vacuum condition. Recently, this limit has been overcome by the realization of Liquidphase electron microscopy (LP EM), a technique that enables the analysis of samples not withstanding the vacuum. Therefore, LP EM paired with a camera with a very high frame rate allows tracking the motion and the evolution in time of particle in liquids and its dynamic processes.

The motion of the particle together with the presence of liquid significantly affect the quality of the images. Therefore, in order to be able to derive useful information about samples, the images have to go through postprocessing algorithms. First, noise has to be reduced from the original image. However, the more the noise is reduced, the less the details in the image. Consequently, a sharpening algorithm is necessary in order to restore – or even increase - the high accuracy of details of the image. After all these steps, images result to be less noisy and richer in details than the original ones. At this point of the process, images are ready to be analysed.

The idea at the base of the project consists in taking advantage of the motion of the particles recorded in videos, to overcome one of the main limits of the single particle analysis (SPA). SPA is a technique that uses images of thousands of particles of the same nature, to reconstruct 3D models of the particle itself. Images showing different profiles of the particle are clustered according to a similarity criterion, and put together, but problems may arise when angular orientations have to be assigned. Therefore, in order to solve this problem an a priori model can be used to facilitate the orientation assignments. 2D images are compared to the projections of the a priori model set in input, and as result an angular displacement is assigned to each profile. Consequently, the goodness of the a priori model inevitability biases the final result of the reconstruction. In this work, this limit is overcome by merging single particle analysis techniques with the dynamics of particles. Different particle profiles will be registered not only in single frames, but also across the videos, offering a very wide range of orientations. The angular orientation of each profile will be derived by tracking the evolution in time of the motion of each particle, and a priori models will no longer be needed.

In this scenario, the postprocessing phase assumes more and more importance inside the general algorithm, since sharpening single images can lead to uncover very specific features, useful to track the direction of the rotations. Furthermore, this project eliminates any boundaries to a priori knowledge and can be applied to a very wide range of particles.

Monodisperse gold nanorod for high-pressure refractive index sensing

Camino Martín-Sánchez,[a] Guillermo González-Rubio,[b,c] Paul Mulvaney,[d] Andrés Guerrero-Martínez,[c] Luis M. Liz-Marzán,[b,e] Fernando Rodríguez[a]

[a] MALTA, DCTIMAC, University of Cantabria, Facultad de Ciencias, Av. Los Castros s/n, Santander, Spain
[b] CIC biomaGUNE and CIBER-BBN, Paseo de Miramón 182, 20014 Donostia-San Sebastián, Spain
[c] Departamento de Química Física, Universidad Complutense de Madrid, Av. Complutense s/n, 28040 Madrid, Spain
[d] ARC Centre of Excellence in Exciton Science, School of Chemistry, University of Melbourne, Victoria 3010, Australia
[e] Ikerbasque, Basque Foundation for Science, Bilbao 43018, Spain
Contact: martinsc@unican.es

Abstract

This work investigates the surface plasmon resonance (SPR) of monodisperse gold nanorods (AuNR) aqueous solutions (10^{11} NP/cm^3) under high-pressure conditions. We show that the longitudinal SPR of AuNR (aspect ratio: 3.4) redshifts with pressure as a consequence of two competing effects: a blueshift induced by the increase of electron density due to AuNR compression, and a large redshift due to increase of the solvent refractive index [1]. Here we show that the LSPR pressure redshift can be explained within the Mie-Gans model [2] by changes of the refractive index *n* of the surrounding medium. These measurements unveil the suitability of AuNRs for refractive index sensing and detection of structural changes (water→Ice VI→Ice VII) as it is shown in Figure 1. The so-obtained *n*(*P*) data are compared with those measured by standard interferometric and spectroscopic techniques at high pressure [3]. We will show similar results using AuNR dispersed in methanol-ethanol mixtures, which enable us to widen the hydrostatic pressure range of the transmitting medium up to 11 GPa [1]. Interestingly, high-pressure induced solvent solifification yields notablt changes in the AuNR plasmonics.

We acknowledge finantial support from MINECO (MAT2015-69508-P, MAT2017-86659-R, MAT2015-71070-REDC).

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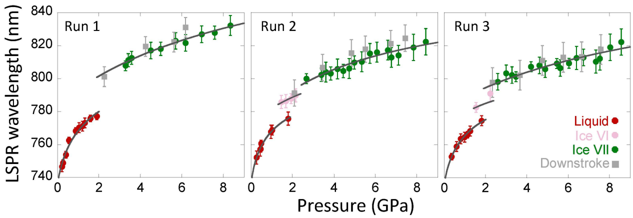

Figure 1: Pressure dependence of the LSPR band of AuNRs in aqueous solutions. The plots include experimental (filled circles) and calculated (solid lines) values of $\lambda_{\mathrm{LSPR}}(P)$ using the Mie-Gans model.

Substrate material study for the growth of Multi-Layer Graphene Nano-Walls

Arevik Musheghyan Avetisyan, Roger Amade, Jose-Luis Andujar, Esther Pascual and Enric Bertran-Serra

ENFOCAMAT(FEMAN) Group, IN^{2}UB, Dep. Applied Physics, Universitat de Barcelona,
C/ Martí i Franquès, 1, 08028 Barcelona, Spain
amusheghyan91@ub.edu

Abstract

Multi-layer graphene nanowalls (MLGNWs) can be grown on any type of substrates without catalyst as long as the substrate can sustain the growth temperature, which is typically between 600-800°C. Among the several deposition techniques for synthesizing MLGNWs films, ICP-CVD is one of the most promising techniques because of its potential for low temperature synthesis. Plasma growth of graphene provides a rich chemical environment, including a mixture of radicals, molecules and ions from a simple hydrogen-hydrocarbon feedstock thus allowing for lower deposition temperatures and faster growth. The MLGNWs initial growth contains at least two nucleation stages. The first nucleation provides a buffer layer formation, which is one of the main prerequisites for getting a good quality MLGNWs with significant growth rate. This first buffer layer usually contains a high number of defects like amorphous carbon, which depend on the substrate material. After the formation of the first buffer layer, secondary nucleation and vertical alignment of graphene nano-sheets occurs, which is similar for all types of substrates. A slight change in some of the processing parameters (gas composition, precursor gas flow, temperature, pressure and plasma power) can alter the first nucleation process, but has no effect on the second nucleation.

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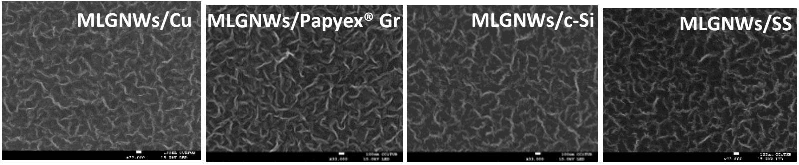

Figure 1: SEM images of MLGNWs grown on various substrates(Cu foil, Papyex® Gr, c-Si and SS 304)

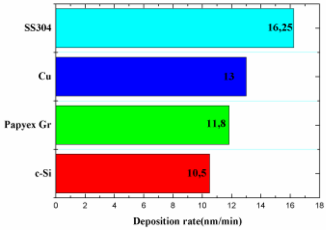

Figure 2: Deposition rate for different substrates

Facile, fast and high reproducible method for nanocrystals coupling to carbon nanotubes

J. Oliveras, M. Ventosa, J. Patarroyo, C. Gimbert, A. Llobet, N. Bastús, V. Puntes
Institut Català de Nanociència i Nanotecnologia (ICN2), C/ Serragalliners s/n (UAB Campus), Bellaterra, Spain
Contact: jana.oliveras@icn2.cat

The future carbon-free energy scenario is moving towards the sustainable production of solar fuels based on artificial photosynthesis. This technology biomimics natural photosynthesis by capturing and storing energy from sunlight in chemical bonds, for instance, by splitting water into $H_2$and O. The success of this complex process is thanks to the multicomponent architecture of the natural enzymes. Inspired by the specifically engineered natural system, the SOLHYCAT project was designed with the aim of producing an artificial catalyst for water splitting, which components have been preciselyselected according to its function within the photochemical process. It is based on the junction between inorganic semiconductor nanoparticles (NPs) and a molecular catalyst (molCAT) through conductive carbon nanostructures (CNs). The NPs act as photoabsorbers, with controlled structure for efficientlightabsorption, electron-hole generation, band alignment and stable interface with the CNs. The latter has a key role as platform to anchor the molecular catalysts, which are responsible for the fast chemical reactions.

For decoration of CNTs we use an approach based on the incubation of NCs with CNTs being destabilized by change of the solvent polarization by using toluene, resulting in a controlled deposition of the previously synthesized semiconductor NCs. In this survey, several semiconductors such as Ag_2S[1], TiO_2 brookite and anatase[2], CdSe and CdSe@CdS[3] were synthesized and coupled to Single-Walled CNTs (SWCNTs) with positive results. This approach has proved in water destabilizing the NPs by dyalisis. Obtained results were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) or scanning transmission electron microscopy (STEM), prior and after incubation (Figure 1 and Figure 2 respectively), proving it to be fast, straightforward, highly reproducible and easily scalable.

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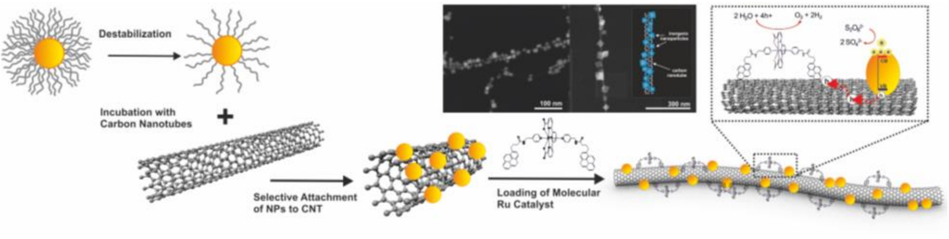

Figure 1: SOLHYCAT Scheme. Left: synthesis of decorated CNS with semiconductor nanoparticles. Right: molecular catalyst for direct and stable attachment to CNS.

Carbon based materials growth process effect on 304 stainless steel substrates.

Fernando Pantoja-Suárez[1,2,3], Islam Alshaikh[1,2], Joan Martí-González[1,2], Arevik Musheghyan-Avetisyan[1,2], Roger Amade [1,2], José-Luis Andujar[1,2], Esther Pascual[1,2] and Enric Bertran-Serra[1,2]

[1] ENPHOCAMAT (FEMAN) Group, Dep. Applied Physics, Universitat de Barcelona, C/ Martí i Franquès, 1, 08028, Barcelona, España

[2] Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona

[3] Departamento de Materiales, Facultad de Ingeniería Mecánica, Escuela Politécnica Nacional, Ladrón de Guevara, E11-253, Quito, Ecuador

fpantoja@ub.edu

Carbon based materials have earned a well-deserved reputation. Thanks to their physical, chemical, electronic, thermal, mechanical and optoelectrical properties, research and industrial groups all over the world are constantly improving their production. They are a versatile material that can be obtained by different ways. In addition, flexible displays, sensors, and energy storage devices can be manufactured using this kind of material. The development of energy storage devices is one of the applications in which carbon-based materials, as carbon nanotubes (CNTs) or graphene nanowalls (GNWs), stand out. Another interesting aspect of these materials is that they can be obtained on conductive materials, such as nickel, copper or steel. The last one is precisely one of the substrates that we and other research groups have selected to support the carbon-based materials. In a hydrogen-rich atmosphere, at temperatures in the range 600 to 730 °C, with the use of precursor gases (acetylene or methane) and using plasma technology, uniform forests of these structures have been obtained on the surface of 304 stainless steel. However, the growth process can produce counterproductive effects on the steel substrates. Above all, decrease its flexibility, increase the crystal size or decrease its corrosion resistance. In that way, we believe it is appropriate to present some of our results observed in 304 stainless steel during our experiments. SEM images, XPS analysis and XRD allowed us to document changes in the surface and also in the bulk material.

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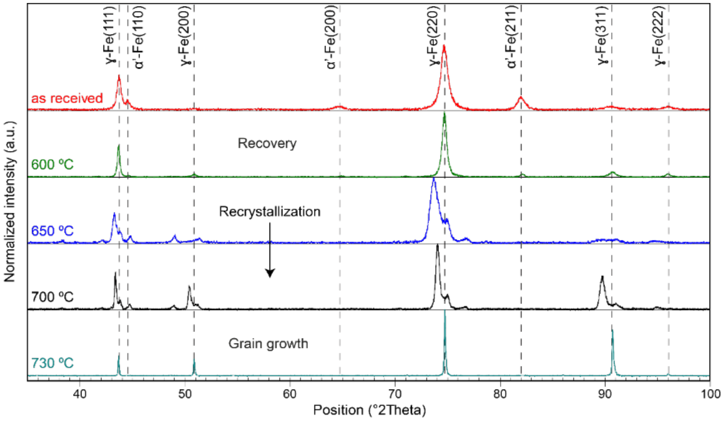

Figure 1: XRD patterns of untreated and reduced samples of 304 stainless steel at 600, 650, 700 and 730 °C

Real-Time Interferometric Aptasensor for Thombin in Nanoporous Anodic Alumina

L. Pol, L.K. Acosta, E. Xifre-Pérez, J. Ferré-Borrul, L.F. Marsal

Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, ETSE, Universitat Rovira i Virgili
lluis.marsal@urv.cat

Aptamers have been reported as a promising class of compounds for biosensing since their 3D structure leads to bind a wide variety of biomolecules and permit detection down to the femtomolar range. Aptamers are single-stranded nucleic acid molecules that bind with high affinity and specificity to their target. The thrombin binding aptamer is one of the mostly studied aptamers in aptabiosensors [1].
Nanoporous anodic alumina (NAA) has been reported as an assuring material to use as a biosensor platform because of its advantageous optical properties [2]. Such properties are exploited in Reflection Interference Spectroscopy (RIfS) for optical biosensing [3]. For such application. the surface chemical functionalization is a crucial step.
In this work, we propose a path for the NAA surface functionalization by the attachment of Thrombin – Binding-Aptamer (TBA) to the pore walls, as illustrated in Figure 1a. By means of RIfS in a flow cell system, we study the binding events during the functionalization progression and the ability of the system to detect the thrombin.
In order to achieve aptamer functionalization NAA is modified in a first step by grafting aminopropyl triethoxysilane (APTES). The second step consists on the covalent attachment of sulfo-NHS-biotin by the formation of amide bond and in the third step the biotin-modified NAA is exposed to streptavidin. Next step is grafting the biotinylated thrombin binding aptamer (TBA) to the streptavidin. Finaly the aptamer modified NAA is exposed to diferent concentrations of thrombin. Figure 1b shows an example of the detection of thrombin at 50 µg/ml concentration. We demonstrate the ability of the system to detect all the binding events during the NAA surface functionalization to achieve an aptasensor against thrombin. We also prove that the system is able to specifically detect thrombin.

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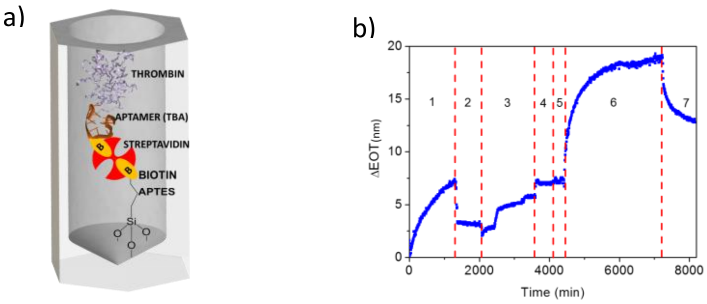

Figure 1: a) Schematic of NAA surface functionalization b) Example of registered change in EOT as a function of time during the NAA functionalization and aptamer-mediated thrombin detection: 1) Sulfo-NHS-Biotin 5 mM, 2) PBS, 3) streptavidin 50 µg/ml, 4) aptamer (TBA) 10mM, 5) PBS, 6) Thrombin 50 µg/ml, 7) PBS

In-Situ Liquid Electron Microscopy for Imaging Proteins and Polymer Assemblies in their Native State

Lorena Ruiz Pérez[1,2], Cesare De Pace[1,2], Gabriele Marchello[1,2], Neil Wilkinson[3], and Giuseppe Battaglia [1,2,4,5]

[1] Department of Chemistry, University College London, 20 Gordon Street WC1H 0AJ, UK.
[2] The EPSRC/Jeol Centre of Liquid Electron Microscopy, University College London WC1H 0AJ, UK.
[3] Gatan UK, 25 Nuffield Way, Abingdon OX14 1RL, UK.
[4] Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute for Science and Technology (BIST), Barcelona, Spain. [5]Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain
l.ruiz-perez@ucl.ac.uk

Electron microscopy (EM) is one of the most powerful techniques for structural determination at the nanoscale, with the ability to image matter down to the atomic level. The short wavelength associated with electrons is pivotal for achieving high resolution. Electrons interact strongly with matter hence electron microscopy is only possible by keeping the beam under high vacuum in order to avoid undesired scattering events in the beam path. High vacuum comes at the expense that the EM samples conventionally must be in the solid-state. This means that samples in liquid form or containing liquids- especially water- require special preparation techniques involving either controlled drying or cryogenic treatments, which often alters the microstructure and chemical nature of the sample. Such alterations become particularly critical for biological samples and soft materials where meso- and nano-scale structure are controlled by the presence of water (and/or other liquids). While some of these limitations can be overcome using fast vitrification processes to solidify liquid samples, vitrified water is not liquid water and its structure and hydrogen bond network is very different. Even so, cryogenic TEM is still limited to providing static snapshots, and does not allow **dynamic observation**. An efficient approach for TEM imaging of materials in liquid form is achieved by encapsulating the liquid sample within electron-transparent materials such as graphite foils , silicon nitride films (Si_3N_4) , ionic liquids or graphene sheets which form a barrier between the liquid medium and the high vacuum of the microscope column.[1] We now have the possibility of using **Liquid TEM (LTEM)** to study nanoscopic structures within liquids and monitor dynamic processes. This approach offers a step-change in our ability to study matter in its “virgin-state” on the nano and micron scale, removing the artifacts induced by drying or cryogenic treatments.

We investigate two different soft organic systems in liquid state *in-situ* (i) a polymer assembly with a localised asymmetry , and (ii) the well known ferritin protein. Both systems were imaged over time with a high frame-rate- acquisition direct detection camera, the K2-IS from Gatan. The ultra-high sensitivity of the K2 allows low-dose imaging modes limiting considerably electron dose damage and facilitating high spatial and temporal resolution.[2] Particles were imaged displaying brownian translational and rotational motion withour the need for staining agents. A high variety of particle profiles were then acquired over time for both systems (i) the polymer assembly and (ii) the protein ferritin hence making time a fundamental element of the particle 3D reconstruction process. These findings set the foundation for future time-resolved 3D structure reconstruction of unlabeled soft organic materials in their native environment. Moreover our results open a new avenue for next generation biological *in-situ* TEM.

This study was accomplished using a Jeol JEM 2200FS equipped with an in-column omega filter in combination with the *in-situ* K2-IS camera from Gatan. The *in-situ* liquid TEM holder used was the Ocean holder from DENS solution.

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Gelatin-hydroxyapatite hybrid hydrogels as composite scaffolds for bone tissue engineering applications

S. Vílchez, X. Garcia, J. Esquena

Institute of Advanced Chemistry of Catalonia (IQAC-CSIC), and Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Barcelona, Spain.

susana.vilchez@iqac.csic.es

Nowadays, demands for artificial biomimetic materials in medical field are becoming more frequent. Researchers have evaluated various biomaterials to mimic the specifically organized nanoscale structure of the bone. Among those, composite materials of hydroxyapatite crystals and natural polymers (collagen and gelatin) have received a great deal of attention [1-4].

In this work, the design and the preparation of a gelatin-hydroxyapatite (Gel-HAp) hybrid hydrogel, as a macroporous scaffold for hard tissue engineering applications, is reported. Microbial transglutaminase (mTGase) has been used to form biocompatible and thermally stable hydrogels from gelatin. An experimental design was carried out to explore the effects of gelatin and transglutaminase concentrations on hydrogel properties. Subsequently, hydroxyapatite (HAp) powder was synthesized by a sol-gel technique. Microstructure of the calcined hydroxyapatite was examined by means of scanning electron microscopy (SEM), and the material was characterized by X-ray diffraction and Fourier transformed infrared spectroscopy (FTIR) before incorporating it on cross-linked gelatin hydrogels. Rheological, morphological and physicochemical properties of the Gel-HAp composite hydrogels were examined, as well as their absorption equilibrium values, in order to evaluate the effects of HAp incorporation.

The results revealed that both elastic modulus and absorption ratio depend on gelatin and enzyme concentrations. The incorporation of HAp into gelatin hydrogels induced an increase of their elastic modulus. Thereby, these findings suggested that the synthesized composite materials might be potentially useful in hard tissue regeneration and tissue engineering fields.

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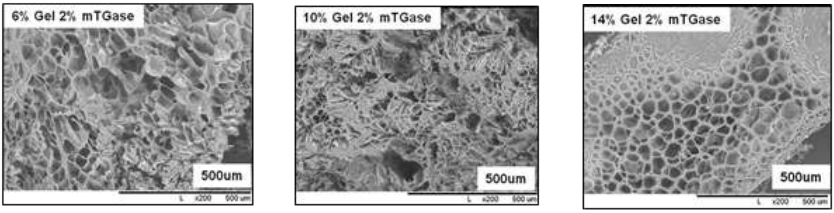

Figure 1: SEM morphologies of gelatin-HAp composite foam at different gelatin concentrations.

Polyphosphorhydrazone PROXYL radical dendrimers

Songbai Zhang, Vega Lloveras and José Vidal-Gancedo

Institut de Ciència de Materials de Barcelona ICMAB–CSIC; Campus UAB, 08193 Bellaterra, Barcelona (Spain) and CIBER-BBN, Barcelona (Spain)
E-mail: szhang@icmab.es

In our group we are focused on the study of molecular materials based on radical dendrimers, their magnetic properties as well as their biomedical applications.[1]

Here we describe the synthesis and EPR study of different generations of PROXYL terminated Polyphosphorhydrazone (PPH) radical dendrimers. The interaction between pendant stable radicals at the exterior of the dendritic surface and their dynamic behaviour can be studied by Electron Paramagnetic Resonance (EPR) spectroscopy. This is important to understand the magnetic properties and other ones like relaxivity of these functionalized dendrimers. The properties of the radical dendrimers depend on the core dendrimer, the size (generation of the dendrimer), the radical and the linker between the radical and the dendrimer branches. Using lysine as a spacer to bind the radical to the dendrimer, we increase the water solubility of the molecule, something important to keep in mind if we are thinking about biomedical applications.

The synthesis of the radical dendrimers have been followed by several spectroscopic techniques: ^{1}H NMR,^{13}C NMR, ^{31}P NMR, FT-IR, SEC-GPC and EPR, showing the successful synthesis of different generations of Polyphosphorphydrazone.

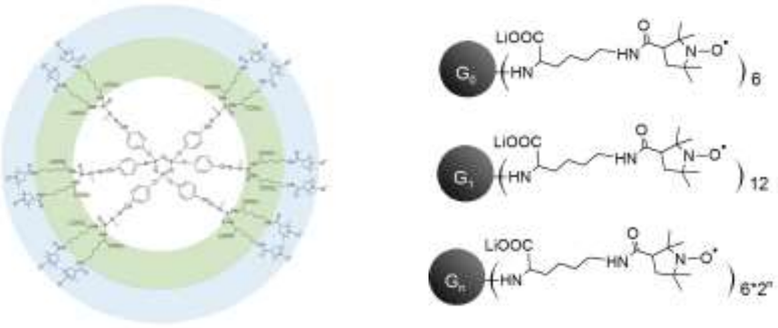

Figure1: Schematic structure of radical dendrimer

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Valorization of residual extract of hydro- distillation process for obtaining silver nanoparticles: Potentialities as antimicrobial agent against Xanthomonas axonopodis pv. phaseoli.

María del Carmen Travieso[1*], Annie Rubio[1*], Mylene Corzo[1**], Cecil González[1*], Oriela Pino[1*]

[*]Chemical- Ecology Lab.[**]Plant Bacteriology Lab. Plant Health Division.
[1]National Center for Animal and Plant Health (CENSA), Apartado 10, San José de la Lajas; Mayabeque, Cuba
mcarmen@censa.edu.cu

The synthesis of metallic nanoparticles (MNP) using noble metals such as silver, has become a practice used to obtain promising nanostructures for different purposes (industrial, biomedical, agriculture, etc.), because they have optical, electrical, magnetic and thermal properties, that confer them behaviors and biological activities, in some cases, different to the individual systems that compose them. Numerous studies have shown their antimicrobial properties. The synthesis of silver nanoparticles (SNP) from plants constitutes a simple, fast and environmentally safe route. Numerous plant species have been reported with positive results for this purpose. In the present work, the residual aqueous extract of the hydrodistillation process of the essential oil from Thymus vulgaris L. was evaluated as a possible source of reducing and stabilizing agents to obtain SNP, as well as the start of the evaluation of the antimicrobial activity against Xanthomonas axonopodis pv. phaseoli. Preliminary results showed that the evaluated extract is promise for the green synthesis of SNP, also it showed antimicrobial activity similar to other silver ionic form and superior to the copper forms evaluated as positive control, which suggests the need for the continuation of the physical-chemical characterization studies and biological evaluations that will make possible the use of this abundant residual.

Key words: Silver nanoparticles, Thymus vulgaris, Xanthomonas axonopodis pv. phaseoli, antibacterial activity, valorization, aqueous residual

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Phantoms Foundation

Alfonso Gomez 17
28037 Madrid - Spain

info@phantomsnet.net
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