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## Abstract book



Materials Science PhD program

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# Oral presentations

## Giant Negative Electrocaloric Effect with Antiferroelectrics

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Antiferroelectrics are characterized by an antiparallel arrangement of electric dipoles that results in spontaneous zero net polarization but can be switched into a polar state with an external electric field. They have not been as researched as their ferroelectric counterparts because the non-polar ground state makes them less obvious for applications; however, they do have some very interesting and potentially useful properties. One of them, which will be presented here, is their anomalous (negative) electrocaloric effect, whereby antiferroelectrics cool down when a voltage is applied to them.

The electrocaloric effect is desirable in electronic applications for less bulky and more efficient and durable cooling systems, without the need of moving parts and with higher temperature changes than other solid-state cooling approaches like thermoelectrics. We have examined the response with an infrared camera close to and beyond the Curie temperature for the archetype antiferroelectric PbZrO<sub>3</sub>. The results show a giant negative electrocaloric effect propagating across the sample like a cold front and yielding a record-high figure of merit  $|\Delta T|/|\Delta E|$ . We have also observed a negative-to-positive electrocaloric transition arising from structural changes, providing further ways for a more versatile cooling system.

## **Advanced 2G HTS Tape Architectures for HVDC Superconducting Fault Current Limiters**

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The most advanced solution for the gradual incorporation of renewable energy production far from consumption centers is the HVDC Supergrid. Yet, the current fault issue for DC operation is more critical when compared to AC grids. The main bottleneck comes from the fact that the current cut during a fault is much more difficult since there is no zero crossing of the signal. The DC circuit breaks for this kind of conditions are very expensive and most are still limited in terms of maximum current. In this scenario of demand for cost/efficiency in protection, the Superconducting Fault Current Limiter (SFCL) fits as a preeminent solution due to its intrinsically fast actuation. However electrical performance limitations related to the thermal properties of today's 2G HTS commercial tapes makes the SFCL economically undesirable for high voltage operation due to an excessive length of tape needed. In this scenario, FASTGRID aims to boost the thermo-electrical properties of HTS tapes to overcome the economical disadvantages and build a HVDC SFCL.

# Nanostructured Back Reflectors for Efficient Colloidal Quantum Dot Infrared Optoelectronics

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The efficient absorption and optoelectronic conversion of infrared radiation is of interest in both sensing and energy harvesting. A significant fraction of the solar spectrum (>17%) in the IR is not captured by current photovoltaic technologies such as crystalline silicon (c-Si), which has an indirect bandgap of 1100 nm.

Colloidal quantum dots (CQDs) are attractive materials to convert IR photons into electricity. They exhibit a strong and tunable absorption in the IR and can be easily processed at low temperatures on various substrates. Unfortunately, full IR absorption requires  $\sim\mu\text{m}$ -thick CQD solids, beyond the diffusion length of photoexcited charges in these materials ( $\sim 300$  nm), curtailing the photoelectric conversion efficiency.

Light-trapping strategies could potentially overcome this limitation by enhancing light absorption in a given CQD volume; however, this often comes at the expense of worsened electrical transport and increased surface recombination when the charge extraction layers are modified.

Here we report physically malleable (soft) photonic electrodes enable us to enhance IR photon harvesting, for they permit us to nanostructure the imprintable hole transport layer (HTL) while maintaining excellent electrical properties (high hole mobility and low surface recombination). Specifically, we replace conventional rigid HTLs with a soft, moldable HTL that combines the mechanical and chemical requisites for high-finesse nanoimprint lithography; and the mobility and energy levels enabling the incorporation of IR photonic features and efficient charge extraction.

We design the photonic electrode to enhance IR absorption beyond 1100 nm and then implement this design using soft nanoimprint lithography on the new HTL layer. Only as a result, we achieve a record photon-to-collected-electron efficiency (EQE) of 86% at 1220 nm.

## **Band gap tuning of solution-processed ferroelectric perovskite $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ thin films**

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The use of ferroelectric perovskite oxides as a stable photoactive layer has opened up a ground-breaking new arena of research. They present an alternative ferroelectricity-related mechanism for solar energy conversion that could surpass the fundamental efficiency limits of conventional semiconductors. Unfortunately, most ferroelectric perovskite oxides are wide-band gap materials.

Herein, we perform a novel elemental composition engineering of ferroelectric perovskite  $\text{BiFeO}_3$  (BFO) by substituting Fe by Co cations, as a means to tune the characteristics of the transition metal-oxygen bond and ultimately the band gap. We demonstrate by solution processing the formation of epitaxial, pure phase, and stable  $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$  (BFCO) thin films, with tuned band gap from 2.7 eV of BFO to 2.3 eV for  $x=0.3$ , while preserving the ferroelectricity. [1] Vertical devices pursuing a simple and oxide-based heterostructure with  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  and FTO as conductive electrodes are fabricated to demonstrate the potential of this class of material for photovoltaic applications. Photocurrent response in the visible region (J-V curves, quantum efficiency) show improved results for BFCO phase with respect to unsubstituted oxide.

Overall, the BFCO system is a potential photoactive material and will provide a robust platform to study the underlying physical properties of these systems. Also, the band gap tuning possibilities could also offer new opportunities when combined with other conventional photovoltaic devices.

### References

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## Combined photo- and thermocatalytical approach for efficient CO<sub>2</sub> hydrogenation

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Recycling of carbon dioxide to renewable fuels using green energy sources is an urgent and challenging task. Out of all reactions, CO<sub>2</sub> methanation still attracts a lot of interest due to its favorable thermodynamics and potential application in chemical energy storage. Up to date, Ni supported by CeO<sub>2</sub> remains the most widely used material for CO<sub>2</sub> methanation due to its high activity and availability. Nevertheless, the working temperature for carbon dioxide hydrogenation in presence of this catalyst is relatively high. Another uprising field for CO<sub>2</sub> reduction is LSPR (local surface plasmon resonance)-enhanced catalysis. Owing to the fact that Ni exhibits a plasmon resonance under visible light illumination, it may result in increasing of its catalytic activity towards CO<sub>2</sub> reduction. In this work, we used a photothermal approach in order to study the combined effect of temperature and light on the carbon dioxide hydrogenation over the high-surface-area Ni-CeO<sub>2</sub> catalyst.

Mesoporous silica template was used in order to obtain high surface area CeO<sub>2</sub> support with Ni clusters by wet impregnation. As an alternative support shape, we have grown a porous CeO<sub>2</sub> structure in a shape of “nanoleaves” by electrodeposition on Cu and Ni substrates, with a possibility of upscaling. EDX and XRD characterization proved a crystalline structure of a grown support.

Plasmonic nickel nanoparticles of different sizes and shapes, such as spheres and rods, were synthesized in order to compare their light absorption in different ranges. We have seen that the spheres of various sizes tend to absorb in the UV range, while the elongated Ni nanoparticles have a peak in the UV and a broad band in the visible range. Its broadness may be explained by a big variety in sizes of obtained nanoparticles.

The hybrid catalysts were tested in a specially designed flow-type reactor, which allowed simultaneous heating and illumination of the catalyst. We have observed conversion of CO<sub>2</sub> to methane starting from 250°C, which significantly increases under UV light illumination. The effect of light might have two explanations: absorption of UV light by ceria and effective light extinction by Ni nanoparticles due to LSPR. Further studies will be focused on separating the contributions of plasmonic Ni nanoparticles and light absorption by ceria, as well as synthesizing Ni nanoparticles with plasmon resonance maximum at the visible light range for future applications based on solar light utilization.

## **Tuning Quatsome vesicles for biomedical applications**

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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. These non-liposomal charged bilayer vesicles, which we have termed Quatsomes, presents different properties as changing its components or medium and can be precisely decorated or tuned with multiple targeting groups in order to fit better to the needs.

The aim of this study will be to show the main characteristics of different systems of Quatsomes and their high potential of applications in nanomedicine, such as bioimaging and blood stability. Composition changes using other surfactants or cholesterol derivatives will change its size and surface charged density so we could obtain high positively charged vesicles, almost neutral vesicles and negatively charged vesicles, changing the Quatsomes properties.

Quatsomes can also be tuned in order to get new characteristics. The addition of organic fluorescent molecules can give us new bioimaging applications and its pegylation can decrease its toxicity in the bloodstream empowering its applications as nanocarriers.

## **Graphene based electrodes for retinitis pigmentosa diagnosis**

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Graphene has proved to be an outstanding material for the fabrication of biocompatible electrodes and multi electrode arrays (MEA). Motivated by their high sensitivity, low noise, scalability and stability in aqueous electrolyte, graphene based MEA have been used for the detection of relevant molecules and biomolecules as well as electrical cell signals, either in vivo or in vitro. Armed with these tools we are now able to shed new light onto several diseases and pathologies.

One particular field on which this technology can be useful is on the retinitis pigmentosa diagnosis. Retinitis pigmentosa is a degenerative disease that causes the loss of photoreceptor cells on the retina producing night blindness and a progressive loss of the visual field. Affecting 1 in 4000 people, retinitis pigmentosa has its onset in childhood, it is generally inherited from the progenitors and involves mutation in at least one of more than 50 identified genes.

One of the possible diagnosis is to follow the degeneration performing electroretinography (ERG). This technique involves placing an electrode on the cornea, flashing the eye with light and recording the electrical signal produced by the retina. Usually, a metal electrode bended in a loop or a contact lens with attached wires are used. These types of electrodes mainly present two problems: discomfort produced by the rigid materials they are made of and the impossibility to measure signals from the whole cornea, since their opacity would block the light meant to stimulate the retina. Therefore, electrodes combining flexibility and transparency could provide an exceptional solution for ERG measurements.

On this work we present the fabrication and characterization of such devices, as well as their use diagnosing retinitis pigmentosa on a P23H rat model. Despite its smaller size, transparency and flexibility, the graphene electrode performs admirably well, enabling the diagnosis of the disease as good as its bulkier, more uncomfortable gold counterpart. Furthermore, the graphene device shows better resolution when dealing with the high frequency components of the ERG signals.

## **Point of care (POC) device with magnetic beads for the fast and quantitative electrochemical detection of Plasmodium antigen**

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Malaria is the parasitic infection with the greatest impact and incidence in the world, with more than three billion people at risk of acquiring it worldwide, and over 200 million infections and 1 million casualties each year. In Spain, the vector mosquito is widely established, 400-600 imported cases are reported annually, and autochthonous cases were reported in 2010 and 2014. In front of this, the professionals of our health system are not familiar with the diagnosis of malaria and lack methods efficient enough for its fast detection. Still nowadays, malaria diagnosis depends on classical microbiological methods in central laboratories and the alternative implementation of molecular methods is expensive and require equipment and user training. An erroneous or delayed diagnostic leads to a patient being treated unnecessarily with inappropriate drugs, with the corresponding side effects, putting their lives at risk.

Here, we present the development of an electrochemical Point-of-Care (POC) device for the fast, simple and quantitative detection of Plasmodium falciparum lactate dehydrogenase enzyme (PfLDH), the parasite responsible of the most serious clinical cases and with the highest incidence. This POC entails an optimized single-step immunoassay, performed with magnetic particles and an immuno-modified signal amplifier, which operation is mostly integrated in a single-use paper-based printed electrode. As we show, the sensor affords quantitative detection of PfLDH down to 2.47 ng.mL<sup>-1</sup> in less than 13 min. Compared to the currently available rapid tests, the proposed assay provides quantitative detection with minimal user intervention, which is not afforded by current tests.

## Electrolyte-gated field-effect transistors for protein detection

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Electrolyte-gated organic field effect transistors (EGOFETs) have been investigated recently as a useful means for biological sensing, as they could operate at low voltages in aqueous media and could be made of biocompatible materials.

We are interested in taking advantage of EGOFETs characteristics in order to develop a device for  $\alpha$ -synuclein detection.

$\alpha$ -synuclein is a neuronal protein mainly present in the brain. It is a natively unfolded protein, but it could aggregate due to its dysfunctional regulation. Consequently,  $\alpha$ -synuclein aggregation can be considered a hallmark of the pathogenesis of different neurodegenerative diseases such as Parkinson's disease.

The sensing element of this device resides at the Au gate-electrolyte interface. In fact two different strategies of Au surface engineering have been developed and compared. The validation and standardization of these two protocols have been carried out by using well known techniques such as electrochemistry and Surface Plasmon Resonance (SPR).

The organic semiconductor used for the device fabrication is 2,8-Difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (dif-TES-ADT) blended with polystyrene (PS). The blend is deposited by Bar-Assisted Meniscus Shearing technique (BAMS).

The working progress consists in combining the EGOFET with a microfluidic system paving the way towards the fabrication of simple and cost-effective devices useful for more efficient diagnosis.

# **Plasmonic mechanochromic metamaterial: development of wireless photodetectors**

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Photodetectors based on mechanical actuators rely on the conversion of electromagnetic radiation into mechanical energy and the quantification of the mechanical deformation by complex instrumentation. In this work, we present the design, fabrication and characterization of an innovative concept of radiation sensor based on the combination of a versatile plasmonic absorber and polymeric diffraction grating in the shape of a cantilever array. The electromagnetic radiation is absorbed and efficiently converted into thermal energy, which induces a variation in the deflection angle of the cantilever, thereby producing large colour changes that can be recorded using a conventional camera. This methodology enables a simple, wireless and high-throughput detection of electromagnetic radiation using low-cost materials and fabrication processes.

# CMOS compatible Hf<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> tunnel junction for non-volatile memory application

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With rapid development of information technology in recent years, the demand for non-volatile memory and neuromorphic computing device has made hafnium zirconium oxide an ideal candidate, which stands out not only for its compatibility with CMOS technology but also its excellent ferroelectricity property. Recently, Lyu et al [1] reported the growth of epitaxial films of ferroelectric Hf<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> (HZO) films on suitably buffered Si substrates. Here, we report on the change of conductance of nanometric (HZO) barriers when its polarization direction is reversed by applying an electric field, so called “electro-resistance” (ER). The functional part of the epitaxial heterostructure consists on a La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> (LSMO) layer that will be acting as bottom electrode, a thin ferroelectric Hf<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> layer and a top metallic electrode. Two different metallic top electrodes have been used: Pt and Co. Preliminary measurements have shown that the HZO layer has a large remnant polarization (~20  $\mu\text{C}/\text{cm}^2$ ) [1]. The ER was studied by a pulse mode measurement, which consists on applying a voltage (VW) large enough to set (or reverse) the polarization state of the barrier; a subsequent small voltage signal (VR(t)) is used to collect the current-voltage characteristic I(V) of the junction and to determine its resistance. The shape of the I(V) loop informs on the nature of the charge transport process across the barrier.

The I(V) curves have been collected in devices using Pt and Co electrodes. We have first observed that data can be well described by a direct tunneling barrier model that allows to extract the barrier height and determine its change with VW. Moreover, we observed that Co electrodes results in a larger ER than Pt electrodes, that reaches about 700 % at about VW  $\approx$  4V. However, the ferroelectric polarization loops indicate a coercive voltage of about VC  $\approx$  2 V. If polarization reversal were to rule ER, then one should expect an onset voltage for the ER near about VC. We tentatively propose that an ion-related transport mechanism coexists with the tunnel transport and combine to the measured ER.

## References

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# Water-processable cellulose-based sacrificial layers for advanced nanofabrication

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Cellulose is the most abundant polymer on Earth and for centuries has had a wide technological impact in areas such as textile, packaging or knowledge storage. It is low cost and biodegradable, and possesses excellent mechanical characteristics that have raised the interest of many engineering fields. The versatility of cellulose has recently opened new venues in advanced materials in electronics, energy and biomedical applications. In this work, we combine hydroxypropyl cellulose (HPC), a water soluble and biodegradable cellulose derivate, with nanoimprinting lithography (NIL), the most promising method for mass-produced inexpensive nanostructures over large areas and with a very low density of defects.

Employing the cellulose derivative as NIL resist, all-green advanced nanofabrication processes are achievable. For instance, we are able to pattern silicon wafers or fabricate metallic nanoparticle arrays in a straight forward process that requires only water as solvent. Furthermore, HPC water-soluble sacrificial layers can be also stacked with traditional resists such as Poly(methyl methacrylate), where one of the two materials can be selectively removed by developing in orthogonal solvents. This capability becomes even more interesting by including nanoimprinted layers in the stack, leading to the encapsulation of arrays of air features in the resist.

Finally, HPC membranes can be used as support layer for transfer printing of nanostructured metal electrodes. The cellulose film in fact serves as actual adhesive, allowing us to pick and place thin metallic film from patterned silicon substrate to active devices, obtaining simultaneously the metallic contact and the encapsulation. If necessary, the HPC layer can be eventually dissolved in water, leaving only metallic pattern printed on a target substrate. Interestingly, by simply reiterating this process it is possible to fabricate novel 3D structures made of stacked nanopatterned metallic films that present intense plasmonic resonances and exotic optical properties.

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# Development of transparent conducting oxides thin films grown by pulsed laser deposition

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Transparent conducting oxides (TCO) are pivotal materials for technological applications. The fact that they combine high electrical conductivity and high transparency makes them a crucial element in many devices such as touchscreens, solar cells, defrosting coatings, etc. where they play the role of transparent electrode. Therefore, there is a strong interest for improving their properties as well as for lowering their cost. For instance, the touchscreen of smartphones or tablets, using indium-tin-oxide (ITO) as TCO, constitutes one of its most expensive compounds. This is due to the scarcity of indium resources. It is thus obvious that there is an urgent need for developing alternative materials. [1,2]

Researchers have oriented their interest to highly correlated metals made of transition metal oxides. In this category of TCOs, the high correlations between free electrons lower the plasma frequency (onset of light penetration in the material) below the visible range. As electronic transitions occur at higher energies, high transmittance in the visible is thus guaranteed. On the other hand, the high carrier concentration allows a high conductivity. [3]

Our focus is on two metallic oxides: strontium vanadate SrVO<sub>3</sub> (3d<sup>1</sup>) and strontium niobate SrNbO<sub>3</sub> (4d<sup>1</sup>). In addition of fulfilling the requirements above-mentioned, their perovskite structure also makes them particularly attracting for integration in all-oxide heterostructures. However, the growth of such compounds is made difficult due to the multiple possible valence states of V and Nb.

Here, we report on the methodology adopted to fully characterize and optimize our TCO thin films. It will be shown how a careful optimization of the growth environment could allow us to obtain the best PLD-grown SrVO<sub>3</sub> films ever reported; with resistivity as low as 30  $\mu\Omega\cdot\text{cm}$ , carrier mobility of around 8  $\text{cm}^2/(\text{V}\cdot\text{s})$  and RRR of 11.5, while maintaining high transparency. [4] These values compete with the ones of optimal films grown by molecular beam epitaxy. [3] A comparison with SrNbO<sub>3</sub> thin films will also be provided.

## References

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# Assessment of carbon contamination in MoS<sub>2</sub> grown by MOCVD using Mo(CO)<sub>6</sub> and (CH<sub>3</sub>-CH<sub>2</sub>)<sub>2</sub>S precursors

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This work aims at assessing carbon contamination in large-scale deposition of MoS<sub>2</sub> films by metal-organic vapour deposition (MOCVD). This growth method has shown to produce continuous and homogeneous films of high quality transition metal dichalcogenides. [1] In contrast to conventional CVD using chalcogen and metal oxide powders as precursors, MOCVD is superior in terms of controlled supply of volatile precursors and the high potential for process upscaling and wafer-scale deposition. However, carbon contamination has been shown to be a major issue, if organic chalcogen precursors are used. [2][3]

In this work we demonstrate the growth of MoS<sub>2</sub> films on Si/SiO<sub>2</sub> substrates by MOCVD in a vertical hot-wall reactor using molybdenum hexacarbonyl Mo(CO)<sub>6</sub> and diethyl sulfide (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S. Diethyl sulfide has been identified as the source for undesirable C formation. Based on SEM, Raman and XPS data we discuss how carbon incorporation depends on several growth parameters like temperature, growth time, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S and Mo(CO)<sub>6</sub> precursor flow. We reveal the effect on MoS<sub>2</sub> synthesis with respect to growth rate and evolution of film morphology. Carbon incorporation inhibits lateral growth of MoS<sub>2</sub> domains and leads to photoluminescence quenching. Finally, we discuss an optimized growth parameter set for monolayer MoS<sub>2</sub> and how the carbon footprint can be mitigated by using hydrogen as a reductive gas.

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## Rotational Polarization Nanotopologies in BaTiO<sub>3</sub>-SrTiO<sub>3</sub> Superlattices

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Nanoscale ferroelectric materials are demonstrating a high capability to exhibit non-trivial or exotic polarization configurations under the proper electrostatic and elastic conditions. These polar states may exhibit emerging properties not present in the bulk compounds such as chirality or negative capacitance and are potentially promising for technological applications, such as, for example, ferroelectric memories. Here, using Cs-corrected scanning transmission electron microscopy (STEM), we report the observation of rotational polarization topologies at the nanoscale in (BaTiO<sub>3</sub>)<sub>n</sub>/(SrTiO<sub>3</sub>)<sub>n</sub> superlattices with  $n = 2, 4$  and  $10$ . More specifically, we have observed the transition from a highly homogeneous polarization state (monodomain) to the formation of unexpected rotational nanodomains when increasing the superlattices period from a short one ( $n = 2$  and  $4$ ) to a longer one ( $n = 10$ ). The nanodomains reveal dipole topologies such as vortices or waves, never before observed in BaTiO<sub>3</sub> at this scale.

# Atomic Layer Deposition: from molecular chemistry to nanoengineering functional complex oxides

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Preparation of functional oxide thin films at very low temperatures, over large areas and compatible with low- cost and flexible substrates, offers great industrial potential. Atomic layer deposition (ALD) is a very appealing chemical thin-film deposition method that is unique because it ensures excellent large-area uniformity, conformality, and enables simple and atomic level control of film thickness and composition. Additionally, ALD favors controlling and nanoengineering of interfaces and demanding structures (3D substrates).

The precursor chemistry is one of the main parameters that determines the processing conditions and ultimately the film properties. Despite commercially available ALD precursors, there is an increasing need for new or improved precursors to further enrich the variety of ALD functional oxides, especially multicomponent oxides. Here we explore for the first time the use of a single-source heterobimetallic precursor [1] versus multiple source precursors to stabilize by epitaxial growth GdFeO<sub>3</sub> thin films by ALD, attractive for its potential applications in magneto optical devices. The influence of ligand moieties and ALD process design on the stoichiometry, morphology and phase purity of the deposited films is studied by means of X-ray photoelectron spectroscopy, Scanning Electron Microscopy and X-ray diffraction characterization techniques, respectively.

The combination of novel chemical precursors and ALD opens a plethora of new opportunities to prepare and nanoengineer functional complex oxide thin films at low temperature with enhanced performances.

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## **Control of morphology and polymorphism in organic semiconductor thin films**

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Solution shearing techniques have raised a lot of interest in the field of organic electronics due to the low cost of manufacturing and compatibility with large-area flexible substrates. However, device-to-device reproducibility required for its introduction into consumer electronics still remains quite challenging. A strict control over the kinetic of thin-film deposition is mandatory in order to rule the final coating morphology, microstructure and even polymorphism in case of crystalline materials.

Here, a series of organic thin-films obtained by blending a small molecule organic semiconductor (OSC, Dibenzotetrathiafulvalene, DB-TTF) with an insulating polymer (polystyrene) have been deposited through bar-assisted meniscus shearing (BAMS) technique. This blend has shown excellent electrical properties, stability.

This organic blend processed by BAMS represents an excellent benchmark to study the fundamentals aspects that govern thin film formation and to elucidate the physical processes/interactions involved in such a complex scenario. Our strategy relies on the systematic modification of different experimental parameters, i.e. OSC/polymer ratio, coating speed, temperature or molecular weight, that could modulate final thin-film features. Furthermore, a deep analysis of OFET electrical properties have revealed the strong correlation that exists between morphology and electronic properties.

## Dopant induced structural and electrical changes at the C60F48/pentacene interface

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Doping organic semiconductors (OSCs) with organic molecules to adequately modify their electrical properties is key for device functionality and still poorly understood [1,2]. Recent results have shown that the doping mechanism strongly depends on the electronic coupling between the OSC and the dopant molecule, and consequently, on the structure of the OSC/dopant system [3]. Doping of OSCs is usually achieved by incorporating the molecular dopant into the OSC film. Here we focus on surface doping, where a new p-type dopant from the family of fluorinated fullerenes, namely C60F48, is deposited on the surface of the OSC. The C60F48 molecule has the advantage of low volatility, bulkier shape (to prevent diffusion within the  $\pi$ -stacking of the OSC) and higher thermal stability than other used dopants [4]. Pentacene (C<sub>22</sub>H<sub>14</sub>) has been chosen as benchmark organic semiconductor. The combination of grazing incidence x-rays diffraction (GIXD) and atomic force microscopy (AFM) with photo-electron spectroscopy (UPS/XPS) and Kelvin probe force microscopy (KPFM) allows to correlate the structural properties of the donor/acceptor system with the surface transfer doping mechanisms at nanoscale level. The crystalline quality of pentacene has strong impact on the adsorption and crystalline growth of C60F48 on top. The change in the local surface potential (of up to 0.8 eV) indicates charge transfer and interface dipole formation. The structural properties and thermal stability of the organic-organic interface have been determined by GIXD.

# Nonstoichiometry Driven Ferromagnetism in Double Perovskite $\text{La}_2\text{Ni}_{1-x}\text{Mn}_{1+x}\text{O}_6$ Insulating Thin Films

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In this work we report on the epitaxial growth of  $\text{La}_2\text{NiMnO}_6$  double perovskite thin films on top of (001) oriented  $\text{SrTiO}_3$  substrates by RF magnetron sputtering. The influence of oxygen pressure ( $\text{PO}_2$ ) and growth temperature on the microstructure, stoichiometry of the films, and magnetic and transport properties is thoroughly investigated. It is found that high oxygen pressure promotes the growth of stoichiometric films, with a Ni/Mn ratio almost equal to 1. However, these films exhibit poor ferromagnetic properties with respect to the expected optimum values corresponding to ferromagnetic ordering mediated by superexchange interaction between  $\text{Mn}^{4+}$  and  $\text{Ni}^{2+}$  according to the Goodenough-Kanamori rules. Most interestingly, films grown at low  $\text{PO}_2$  exhibit Ni/Mn ratios below 1, but ferromagnetic properties close to the optimal ones. The valence balance between Ni and Mn ions in nonstoichiometric sample has been elucidated by X-ray absorption spectroscopy. The results indicate that Ni deficiency plays a crucial role in the puzzling insulating ferromagnetic behavior observed in nonstoichiometric samples.

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

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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, as reported in other systems. Previous measurements on the temperature dependence of Spin Pumping and ISHE 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 follows an inverse linear relation with temperature.

# Fully Integrated Electrochemical Sensors: a Disruptive Alternative Compatible With Microelectronics Procedures

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Exhaust gas monitoring in combustion operations is a crucial element for the process control-loop which allows for maximizing the energy output and reducing the emission of pollutants and finds application in many sectors – e.g. coal-fired power plants and automotive. Among the existing sensing devices, solid-state micro-sensors are of great potential interest due to their low cost, small size, fast start-up, low detection limit and quick response – features enabled by means of thin-film technology and mainstream microfabrication processes.

Although there have been many attempts to replace current state-of-the-art bulky sensors, the leaking of oxygen from the reference chamber is still considered the main issue to operate solid-state micro-sensors at the high temperatures required. Besides, many studies on thin-films fabricated by Pulsed Laser Deposition (PLD) or sputtering show the presence of pinholes, which inevitably leads to electrical short-circuit across the electrolyte.

In this study, we report a novel design and fabrication route for a solid-state potentiometric oxygen sensor fully integrated in silicon technology based on a self-sustained YSZ membrane. Two approaches for its hermetic encapsulation are discussed: glass frit sealing for applications up to 600 °C and anodic bonding for higher temperatures. Moreover, we present the characterization of a 20 nm-thick embedded layer of pure tetragonal ZrO<sub>2</sub> fabricated by Atomic Layer Deposition (ALD) that allows for the improvement of the electrolyte reliability by preventing the formation of pinholes.

The proposed system addresses the main limitations of the commercial oxygen sensors and of benchmark solid-state micro-sensors, at the same time allowing for a great flexibility in the selection of the ceramic electrode material and in the design (e.g. the possibility of introducing contact and heating paths), thus tackling some important issues related to the mechanical, chemical and thermal stability of the system.

## **Glass transition in thin film ultrastable glasses: Analyzing the bulk transformation**

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Glasses prepared by physical vapour deposition at substrate temperatures around  $0.85T_g$  present extraordinary thermodynamic and kinetic stabilities, comparable to those of ordinary glasses aged for thousands of years. Due to their improved packing, these thin film vapour deposited glasses transform into the supercooled liquid via parallel growth fronts that initiate at the free surface/interfaces, at least for the first stages of the transformation [J. Phys. Chem. B 118(36), 10795–801, (2015)]. Stability can be further increased by arresting these propagation fronts by capping the surfaces with a higher  $T_g$  material [Phys. Chem. Chem. Phys., 20, 29989-29995 (2018) ]. Using this strategy, the glass transition of these ultrastable glasses takes place via a homogeneous transformation mechanism.

In this work we use quasi adiabatic fast-scanning nanocalorimetry to study the characteristics of this homogeneous mechanism in ultrastable glasses. The results show that the kinetic stability during annealing treatments increases by a factor 25-50 with respect to the uncapped stable glasses. In addition, we also identify the existence of two different glass transition mechanisms. Ultrastable glasses transform both via a rejuvenation process that is compatible with a cooperative mechanism, like the one observed in less stable glasses and via a nucleation and growth-like process which dominates the transformation rate.

## **Inverse spin Hall effect in the metallic oxide SrVO<sub>3</sub>**

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SrVO<sub>3</sub> is 3d metal, with a strong spin orbit coupling making it an ideal candidate for the observation of the Spin-Hall effect (SHE) and its counterpart the Inverse Spin-Hall effect (ISHE). These effects consist in the creation of a spin current via an electrical current (SHE) and the creation of an electrical current via a spin current (ISHE), due to the strong spin-orbit interaction. So far, it has been observed in heavy 5d-metals such as Pt, Ta or W. Using metallic oxides to create spin currents would be a major step in spintronics.

We detected the presence of ISHE in SrVO<sub>3</sub> using a spin pumping system. Using a Co/ SrVO<sub>3</sub> bilayer we excited ferromagnetic resonance (FMR) in the Co, where the spins excited by this effect are pumped through the SrVO<sub>3</sub> via spin pumping effect. The spin pumping is confirmed by the increase of the damping parameter of the Co/SrVO<sub>3</sub> bilayer with respect to a Co single layer. We measured an electrical voltage due to the spin current flowing through the SrVO<sub>3</sub>, confirming the presence of ISHE in this concrete metallic oxide.

# Epitaxial Thin Films of La<sub>2</sub>CoMnO<sub>6</sub> and La<sub>2</sub>NiMnO<sub>6</sub> Ordered Double Perovskites by Polymer Assisted Deposition

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Epitaxial double perovskite La<sub>2</sub>CoMnO<sub>6</sub> (LCMO) and La<sub>2</sub>NiMnO<sub>6</sub> (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<sub>2</sub>BB'O<sub>6</sub> structure.[2]

In this work, high quality epitaxial LCMO and LNMO films were grown on (001) SrTiO<sub>3</sub> 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 μB/f.u. and a T<sub>c</sub>≈230K, thus indicating full cationic ordering of Co<sup>2+</sup>/Mn<sup>4+</sup> in a double perovskite structure (fig. 1). Confirmation 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 μB/f.u. with T<sub>c</sub>≈260K, indicating that the Ni<sup>2+</sup>/Mn<sup>4+</sup> cationic ordering needs to be improved.

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## Exploring nanoporous graphene as a membrane

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The recent bottom-up synthesis of nanoporous graphene (NPG) [C. Moreno et al. | 10.1126/science.aar2009] has uncovered a whole range of new possibilities for 2D materials, both because of the molecular size of the pores as well as their periodic arrangement and the presence of an electronic state that lives inside them. In this work we use Density Functional Theory (DFT) to assess the suitability of this material to build standalone membranes that can effectively filter at the molecular level.

Since a free standing membrane must be able to resist forces that come from multiple sources (differences in gas pressure, vibrations...), a mechanical study is a useful first step to determine whether it makes sense to carry on further calculations. Stress-strain curves for different variations in composition and pore size of NPG show anisotropic behavior of the material from low strain values, as opposed to graphene. The stiffness along a direction is observed to depend mostly on the size of the pores along the respective orthogonal direction. If the size of the pores increases, NPG gets logically weaker to applied stress. In agreement with a recent publication [B. Mortazavi et al. | 10.1016/j.carbon.2019.03.018 ], Young modulus is observed to be up to about a half of that of graphene for the smallest pore size and tensile strength is reduced by a factor of 2 and 3 for the longitudinal and transversal directions respectively. While performing this tests other interesting features appeared, such as substantial and linear variation of the band gap with strain.

The most straightforward use for NPG membranes taking advantage of the molecular size of the pores is to use them as a filter that will allow some molecules to pass while rejecting others depending on both structural and electronic properties. The Nudged Elastic Bands (NEB) method is used to compute energy barriers for different kinds of molecules (H<sub>2</sub>, CO, He, CO<sub>2</sub>, H<sub>2</sub>O...) in their gas phase for different pore structures of NPG. The differences displayed in the values obtained (in the range of 0.1 eV) and their dependence on the specific structure used as a membrane show that NPG can potentially be used to separate different gases from an initial mixture. Moreover, the dependence of this differences on the pore geometry implies that the passage of molecules may be tuned by means of further functionalization.

# **Implementation of the hydrodynamic heat transport model for nanoscale complex geometries using finite elements**

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We present the Kinetic Collective Model (KCM), consisting in the hydrodynamic heat transport equation with ab initio calculated coefficients and the corresponding boundary conditions for interfaces and free surfaces. This model generalizes Fourier transport and can be solved using finite elements to predict the thermal response of electronic devices with complex geometries at reduced length and time scales.

We validate the model by comparing with experimental data on Frequency Domain Thermoreflectance Experiments (FDTR) in Silicon and with the effective thermal conductivity of silicon thin films and holey films.

New phenomenology as phonon viscosity and vorticity arise from the transport equation by analogy with the Navier-Stokes equation for fluids. This approach allows a new physical insight of the Non-Fourier effects taking place at the nanoscale.

## **Analytical modeling of skyrmion-extended defect interaction**

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Magnetic skyrmions are whirling magnetization structures that, due to their small size (few tens of nanometers), high stability and easiness of movement (current densities orders of magnitude lower than those needed to move domain walls) are being considered as highly promising information carriers for a new generation of ultradense magnetic memories and logic devices. The performance of skyrmion-based spintronic devices is affected by the presence of defects in the materials. We present an analytic model for describing the interaction of skyrmions with defects in ultrathin films. The starting point is a Gaussian-like potential of interaction between a defect and a point defect. From this potential, other expressions for the interaction between skyrmions with extended defects, such as line-segments, infinite lines, crossing lines, etc., are found. The dynamics of skyrmions in the presence of such defects, under the driving of polarized current, is studied. We consider several types of torques acting over the skyrmion, either coming from the spin transfer torque with in-plane polarized electrons in the ferromagnet ( $J_f$ ) or from spin Hall-effect induced polarized currents coming from a heavy-metal substrate ( $J_h$ ). If one assumes that the magnetic texture is a rigid quasi-particle, one arrives to Thiele's equation, which describes the motion of the skyrmion. This equation is a non-linear equation whose geometrical interpretation is not trivial. We have rewritten Thiele's equation in the complex plane shows a natural way for expressing all the torques simultaneously into a single vector field, allowing for a complete description of the system with a reduced number of parameters. This expression has a simple geometrical interpretation. For the different types of extended defects we consider, we find the conditions for which dynamic regimes of pinning, guiding, accelerating, or arranging skyrmions by defects can be established. In particular, expressions for the threshold driven current-density to pin or depin skyrmions in such defects, the position of the critical points, as well as the guiding conditions along long defects are found.

# Tunable Circular Dichroism and Valley Polarization in the Modified Haldane Model

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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 ( $\sigma+$  and  $\sigma-$ )] and valley polarization ( $\sigma+$  and  $\sigma-$  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 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).

## References

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# Poster presentations

1.

## **Mechanically soft domain walls in ferroelectrics**

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There is currently a vigorous research effort on the functional properties of ferroelectric domain walls. An important part of their appeal is that domain walls possess functional properties distinct from the host material. Their distinct functionality foment new concepts in electronic nanodevices where domain walls act as mobile two-dimensional elements.

Among the many properties of domain walls, mechanical response appears to have been largely neglected. Our research is focused on the measurement on stiffness of domain walls. In particular, we have used Atomic Force Microscopy to investigate the difference in stiffness between domains and purely ferroelectric (non-ferroelastic) domain walls separating antiparallels 180o domains. Surprisingly, they have a distinct mechanical response, markedly softer than that of the domains they separate.

Initially, Piezoresponse Force Microscopy (PFM) was used to image the polarized domains of the materials and consequently to identify different types of domain walls appearing in the materials. Thereafter, Contact Resonance Frequency (CRF) mode was used to identify the stiffness of the domain walls. In CRF, the stiffness of the material is determined from the measured resonance frequencies of the cantilever when the tip is in contact with the sample, as these contact resonance frequencies depend on the tip sample mechanical coupling and undergo distinct shifts when the tip is scanned over areas with different stiffness.

Theoretical calculations, based also in flexoelectric effects, enhance our experimental results. However, flexoelectricity has a unique intrinsic effect, related to the fact that strain gradients are size-dependent property that scales in inverse proportion to size, therefore flexoelectricity can be huge at the nanoscale, affecting the stiffness of domain walls. Therefore, we also focus on this size effect comparing softness of domain walls in thin films and bulk materials.

2.

## **Enhanced arsenic removal by using sponge-loaded superparamagnetic iron oxide nanoparticles (SPION)**

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In order to remove As(V) efficiently, cube sponge-loaded superparamagnetic iron oxide nanoparticles (SPION) was prepared as an effective sorbent with the advantages of environment-friendly, cheap, easy operating and promising for industrial process. SEM, EDS, XRD and TEM technologies were used to characterize the material. The adsorption behavior of sponge and sponge-loaded SPION under different temperature, initial concentration and contact time were compared. The result showed that with a 2.48% loading mass fraction of SPION, the adsorption capacity of the sorbent increased from 18.73 to 23.97 mg·g<sup>-1</sup> under optimized parameters, increasing 27.98%. All of these indicate that cube sponge-loaded SPION could be effectively used in industry in the near future.

3.

### **Pulse-heating nanocalorimetric studies in CoO thin films**

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The use of membrane-based chip calorimeters has opened the way of studying size dependence of thermodynamic properties in nanomaterials. Among the different calorimetric methods implemented for chip calorimetry, quasi-adiabatic nanocalorimetry reports the best sensitivity per unit area, but do not offers the possibility of measuring heat capacity at constant temperatures as function of other variables (time, magnetic field, pressure...). For this reason, we present a variant of the quasi-adiabatic scanning technique where reducing the current pulse duration to  $\mu\text{s}$  range, the heating is promoted locally (few K) around the base temperature (temperature of the Si frame) and the heat capacity can be evaluated in quasi-static conditions like in AC-calorimetry. The possibility of multiple scan averaging and the huge heating rates accessible (up to 106 K/s) permits to reach exceptional heat capacity resolutions below  $100 \text{ pJ/mm}\cdot\text{K}\cdot\sqrt{\text{Hz}}$ . The method is demonstrated characterizing the antiferromagnetic transition in CoO thin film samples of different thicknesses within the nanometer range. The election of CoO in front of other stable magnetic oxides is due to the large magnetic moment of cobalt and the proximity of its transition  $T_N$  to room temperature that enables engineering applications.

4.

## **Surface modified tungsten oxide nanowires and its application in gas sensing**

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The development of gas sensors that are based on metal oxide nanomaterials (MOx) has attracted intensive research interest in the last years. The most used nano-sized sensing materials are typically wide-bandgap MOx, such as WO<sub>3</sub>, ZnO, SnO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>. MOx at the nanoscale are suitable candidates for gas sensor applications because of their large surface-to-volume ratio that allows high sensitivity and rapid detection of various gaseous species. What is more, gas sensing properties of MOx could be additionally improved by functionalization (or surface modification) with noble metals (e.g., Au, Pt), another MOx (e.g., CeO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>) or organo-functional molecules to provide chemical and electronic sensitization. In my research, WO<sub>3</sub> nanowires have been obtained and functionalized with CeO<sub>2</sub> and APTES (3-aminopropyltriethoxysilane) using aerosol-assisted chemical vapor deposition (AACVD) method. This method has several advantages over traditionally used methods due to its simplicity, relatively low setup and running costs, scalability and possibility of surface modification and incorporation of nanomaterials into a device structure in a single processing step. The synthesized non-modified and modified WO<sub>3</sub> nanowires have been integrated over the active area of the Si-based micromachined transducing platforms fabricated in the Clean Room at the IMB-CNM, CSIC. Gas sensing tests towards relevant analytes such as CO, H<sub>2</sub>, and volatile organic compounds (VOCs) have shown very promising results that will be discussed at the conference together with the physical/chemical properties of the modified WO<sub>3</sub> nanowires.

5.

### **Effectively designed Donor-Acceptor-Donor system containing carborane derivatives for two-photon absorption (TPA) application**

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The two photon absorption (TPA) process is a third-order nonlinear optical process in which materials simultaneously absorb two photons. Materials that exhibit large two-photon cross section can be applied like 3D optical data storage, optical limiting, micro-fabrication, photodynamic therapy or imaging. Considering the general structure of a potentially good candidate for TPA applications and the unique structural as well as electronic characteristics of boron clusters, we propose to synthesize various Donor-Acceptor-Donor system based on carborane derivatives linked to  $\pi$  conjugated fragments. All the compounds are characterized using standard techniques of IR, UV-Visible, fluorescence, NMR spectroscopies and elemental analysis. The main advantages of incorporating boron clusters would be to improve hydrophobicity, low toxicity, thermal and chemical stability among others. The purpose of achieving highly fluorescent materials consisting boron clusters, forecasts to possess large TPA cross sections and are expected to exhibit photoluminescence (PL) properties. This would lead to their prospective application in biomedicine, especially in super-resolution fluorescence microscopy and also in optical limiting. Moreover these compounds might be regarded as potential candidates for anticancer agents for boron neutron capture therapy (BNCT).

6.

### **Novel synthetic route and characterization for AMO<sub>3</sub> (A= Ba, Sr and M = Ti, Hf, Zr) and BaM<sub>2</sub>O<sub>6</sub> (M= Ta and Nb) nanoparticles**

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The role of metal oxide materials has been effusively reported due to their broad range of possible applications such as medicine, materials science and electronic devices. Nowadays the target of being able to control size, morphology, or composition from the metal oxide NPs has raised the interest for further application. Here, we propose a novel, scalable and reproducible synthetic procedure for a wide spectrum of binary metal oxide NPs as AMO<sub>3</sub> (A= Ba, Sr and M= Ti, Hf, Zr) and BaM<sub>2</sub>O<sub>6</sub> (M= Ta, Nb). The general synthetic procedure is based on a solvothermal reaction using a modified polyol route. Small-sized, non-aggregated, crystalline, homogenous and dispersed NPs have been obtained for both type of metal oxide NPs optimizing different parameters. AMO<sub>3</sub> (A= Ba, Sr and M= Ti, Hf, Zr) NPs require a surfactant stabilization (TEG) while on the other hand, the synthesis of BaM<sub>2</sub>O<sub>6</sub> (M= Ta, Nb) NPs was by surfactant-free reaction. Our work, provides a versatile and successful method to prepare AMO<sub>3</sub> (A= Ba, Sr and M= Ti, Hf, Zr) and BaM<sub>2</sub>O<sub>6</sub> (M= Ta, Nb) NPs with full control over its features which represents a new strategy towards the most useful synthetic procedures as sol-gel route. In the case of BaM<sub>2</sub>O<sub>6</sub> (M= Ta, Nb) NPs we achieved a novel method for Ta and Nb oxide NPs being one of the first successful synthesis for these metal oxide NPs from group V compared with the limited references of nowadays. The fast and scalable method developed for this family of metal oxide NPs make them interesting for many applications, focusing on the fabrication of superconducting nanocomposites of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> (YBCO) High Temperature Superconductor (HTS) by Chemical Solution Deposition (CSD) approach. It has been described and demonstrated the enhancement of superconducting properties of YBCO when a secondary phase of a non-superconducting material is introduced in the matrix forming a nanocomposite. The best option to nanocomposite fabrication proved to be the use of YBCO colloidal solutions of NPs having perfect control over NPs size and reactivity. The use and stability of the synthesized AMO<sub>3</sub> (A= Ba, Sr and M= Ti, Hf, Zr) NPs in different types of YBCO precursor solutions, from 100% fluorine (TFA) to low fluorine (low TFA) and non- fluorine (Fluorine-free) was demonstrated. Hence, CSD of colloidal solutions is highlighted as a low-cost route with enhancing of final superconducting properties of the YBCO layers using our as-synthesized nanoscale systems.

7.

## **Molecular functionalization of ferroelectric oxide surfaces**

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Properties of ferroelectric thin films are intrinsically entangled to their surface chemistry, essentially mediated by screening mechanisms trying to compensate bound polarization charges, which produce an electric field opposing the bulk polarization. In general, the orientation of polarization greatly determines the composition of adsorbates present on a ferroelectric surface as well as their sticking coefficients. In the case of thin ferroelectric films, interfacial electrochemical effects can become dominant, creating permanent imprints to bulk ferroelectric polarization or fixing polarization direction. Up to now, focus has been placed on the interplay of adsorbates that normally exist in ambient conditions on ferroelectric surfaces, such as water molecules and carbonates, known to play a critical role as external screening agents as dipole molecules and also by providing ionic species after dissociation. Still, the composition of adsorbates layers in ambient conditions shows a low level of control and reproducibility since it is strongly dependent on the history and storage conditions of the samples and moreover, it leads to remarkable aging of ferroelectric polarization. An alternative to prevent environmental damage of ferroelectric surfaces is to gain control on the adsorbate layer by the molecular functionalization of surfaces, providing the right chemical stability while keeping enough electrochemical reversibility to allow ferroelectric polarization switching.

In this contribution we will show our initial results on BaTiO<sub>3</sub> thin films functionalized with self-assembled layers (SAMs) of organic and electronically active molecules. The combined use of Piezoelectric Force Microscopy (PFM) and Kelvin Probe Force Microscopy (KPFM) enabled us to study ferroelectric properties of thin films and their surface composition respectively. In this sense, we were able to probe the presence of the molecules on the surfaces on the base of KPFM measurements that revealed the difference in work function between functionalized and bare BaTiO<sub>3</sub> thin films. Local hysteresis loops were probed by Switching Spectroscopy PFM (SS-PFM) measurements, whereby an increment of coercive fields of about three times was observed upon molecular deposition. We observed that organic molecules tend to protect the polarization of BaTiO<sub>3</sub> thin films in both directions, while keeping ferroelectric switchability.

8.

### **Influence of rare earth substitution on photoactive BiFe<sub>1-x</sub>CoxO<sub>3</sub> thin films prepared by solution processing**

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In recent years, there has been a worldwide concern for finding alternatives to fossil and nuclear fuels, being solar energy one of the most promising renewable sources to satisfy the global energetic needs. Although commercial Si-based PV devices have been remarkably successful, they present some drawbacks, such as the difficulty to achieve improvements in efficiencies, life and performance in time. Otherwise, an all-oxide PV approach is very attractive due to the chemical, mechanical and thermal stability, robustness and nontoxicity of its elements. Cobalt-substituted ferroelectric BiFeO<sub>3</sub> thin films have aroused great interest as promising photoactive materials for solar energy harvesting although the stabilization of BiFe<sub>1-x</sub>CoxO<sub>3</sub> films with high loads of cobalt have been reported challenging.[1] In this work we will report on the influence of A-site (Bi) substitution by rare earth (RE) cations (Ce<sup>3+/4+</sup>, Y<sup>3+</sup>, Nb<sup>3+</sup>, La<sup>3+</sup>) on the structure, surface morphology and optical properties of solution processed BiFe<sub>1-x</sub>CoxO<sub>3</sub> thin films. We have identified that RE ionic radius, bond dissociation energy A-O and cation electronegativity are critical parameters to understand the benefits of RE substitution on epitaxial growth, surface morphology and improved optical properties of Bi<sub>1-y</sub>(RE)<sub>y</sub>Fe<sub>1-x</sub>CoxO<sub>3</sub> system based on x-ray diffraction, atomic force microscopy, x-ray photoelectron spectroscopy and spectroscopic ellipsometry measurements.

[1] P. Machado, M. Scigaj, M.Coll et al. Chemistry of Materials, 31, 947–954, 2019

9.

## **Fast microwave-assisted polyol synthesis of silver nanoparticles with controlled size**

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The fabrication of different size silver nanoparticles (Ag NPs) by a very fast and simple microwave-assisted synthesis is presented. The Ag NPs are synthesised using polyvinylpyrrolidone (PVP) as reducing, capping and stabilizing agent through a polyol approach. The effects of reaction time, reaction temperature and silver nitrate concentration were studied. Control experiments to study the agitation, the PVP concentration and silver nitrate solvent influences were also prepared. It was found that at short reaction times, at low temperatures and at low silver nitrate concentrations particles are polydisperse and their size is around several tens of nm. However, when these parameters increase their values in a certain range particles experiment a size refinement, decreasing the size up to 10-30 nm and becoming spherical. Above this range, particles first increase their size and then lose the refinement in different ways depending on the reaction parameter. Mechanistic insights to understand the Ag NPs synthetic route here presented are provided based on these observations extract from transmission electron microscopy (TEM) and ultraviolet-visible spectroscopy (UV-Vis) characterisation. Moreover, comprising all these effects allows to control particle size and tune Ag NPs on demand using cross experiment.

10.

## **Thermal conductivity of semiconductor nanowires with bulk-unconventional phases**

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Most bulk semiconductors normally present either zinc-blende or wurtzite phase. Recent developments in nanofabrication, specially in the nanowire growth field, have allowed the access to both phases at normal conditions. In this work, a comparison between bulk-stable and the unconventional phases is conducted for 8 semiconductors, focusing on the physical origin of the ratio between wurtzite and zinc-blende thermal conductivity. Furthermore, we present the results for their nanowire counterparts showing the possibility to tune the aforementioned ratio with the diameter. We find that in the case of AIAs ratio ranges from 1.4 to 0.7 depending on the nanowire diameter, thus making zinc-blende and wurtzite AIAs nanowires attractive systems for complex phononic and thermoelectric applications/systems.

11.

## **Thermal boundary resistance from hydrodynamics model**

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The resistance in heat flux propagation due to the interface between two materials has been an object of study during last years. Nevertheless, present models of this thermal boundary resistance (TBR) as diffuse mismatch model (DMM) do not predict the experimental value. With the kinetic-collective model (KCM) we are able discern the contribution of the TBR from other phenomena due to the hydrodynamics of the heat flux. Then, using values obtained from DMM we are able to reproduce the experiments with small specularities.

Furthermore, with our formalism, we are able to obtain an expression for the TBR depending on the specularity of the interface and intrinsic properties of the materials. In the limit of completely diffusive interface, we recover the DMM expression. All these parameters are obtained from ab initio techniques and are independent of the geometry of the experiment.

These results give the possibility to go further in the study of the TBR without attributing other phenomena to it.

## **Adequate meshing for micromagnetic simulations in systems with cylindrical boundary conditions**

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Micromagnetic simulations in confined geometries are essential to model novel spintronic devices. Adding confinement into micromagnetics implies changing the more convenient periodic or Dirichlet boundary conditions by Neumann's, which are more sensitive to the geometry of the boundary. Micromagnetic simulations are usually done using finite differences in regular hexahedral (3D) or quadrilateral (2D) meshes, which do not fit accurately curved boundaries. This induces numerical error that is critical when the dynamics at the boundaries are relevant. In particular, when simulating thin ferromagnetic disks with a cylindrically symmetric initial distribution of magnetization, and all the external agents are also symmetric, the magnetization should also remain cylindrically symmetric. This can be derived from energy minimization or from the Landau-Lifshitz-Gilbert when assuming cylindrical symmetry. However, quadrilateral meshes used for a disk have rotational symmetry of  $90^\circ$ , which produces a numerical error distribution of the torques with the same symmetry. This distribution of the error breaks the symmetry of the system, and, in long (in time steps) simulations, the accumulation of this error gives rise to non-realistic non-cylindrical magnetic structures with a rotational symmetry of  $90^\circ$ .

We present a new numerical scheme that allows to do micromagnetic simulations in systems with cylindrical boundary conditions and arbitrary magnetisation distribution and perturbations, without neither obtaining artificially stable structures nor increasing the computational power required: a finite differences mesh based in cylindrical coordinates with adaptive polar angle discretization. The proposed mesh has the same symmetry as the boundaries and, with the adaptive polar angle discretization, the numerical error is kept of the same order for both the radial and the angular derivatives. With our numerical method, we are also able to model thin ferromagnetic rings with a central small hole, a case which would result in critical numerical error with a quadrilateral mesh. Additionally, a one-dimensional model is presented for the cases where both the magnetisation distribution and the geometry have cylindrical symmetry. Hysteretic loops in thin ferromagnetic disks and rings with interfacial Dzyaloshinskii-Moriya interaction are simulated to show the convenience of the presented mesh and the potential of thin rings for future applications in magnetic memory devices.

13.

## **AiiDA Workflow for High-throughput computation of Formation Energy**

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AiiDA platform make it possible to perform High-throughput quantum chemical calculations. It is emerging as an effective methodology in computational materials science for the discovery of novel materials and the optimization of selected properties also with virtual screening, promise to revolutionize materials discovery. The AiiDA workflow allows the user to define one or more Processes that (optionally) take some inputs and (optionally) produce some outputs, providing the user as much power to automate tasks while adding features essential for carrying out high-throughput computation. By having a workflow we could automate the formation energy calculation of material with DFT that could help to profiling the concentration of defects (vacancies) in a given material. To do so we write a workflow to investigate the defect formation energy of different configurations in a crystal. We are going to use this workflow with SIESTA atomistic simulation code on yttria stabilized zirconia (YSZ) which is promising material for electrolyte in gas sensors owing to its high ionic conductivity due to oxygen vacancies.

### **C. elegans as a model to assess cardiac function - the case of polypyrrole nanoparticles**

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*Caenorhabditis elegans* (*C. elegans*) are easy to maintain in the laboratory, exhibit physiological and genetic resemblance to humans, possess short life span, rapid reproduction and optical transparency. These qualities has made them an ideal candidate for in-vivo evaluation of nanomaterials [1]. Toxicity of several kinds of nanoparticles (NPs) such as metal, metal oxide, carbon based and silica based nanoparticles are currently investigated using *C. elegans* around the world [2] [3]. However, the toxicity evaluation of polymeric nanoparticles using *C. elegans* is limited [4].

Polypyrrole (Ppy) nanoparticles are conjugated polymeric nanoparticles which are electrically conducting and absorb at the near infrared region. They also disperse well in water, are biocompatible and easy for chemical modifications. Cardiac arrhythmia is a condition where the pumping rate of the heart is irregular (either higher (tachycardia) or lower (bradycardia)) due to disturbance in the electrical propagation. Our particular interest is the electrical conductivity of Ppy that is shown to regulate the irregular electrical impulse of the heart in case of cardiac arrhythmia [5]. Also, the pharynx of *C. elegans* shares similarity with human heart in the pumping mechanism and the presence of calcium ion channels. Studies suggest that *C. elegans* with altered pharyngeal pumping can be used as cardiac arrhythmic models [6]. We propose to evaluate toxicity of Ppy NPs in *C. elegans* and we aim to examine their ability to regulate irregular cardiac pumping by studying the effect of Ppy NPs in pharyngeal pumping of *C. elegans*. To this end, we have synthesized and characterized Ppy NPs and evaluated their ingestion and toxicity on *C. elegans* by assessing survival and phenotypical changes. We are currently investigating the effect of NPs on pharynx pumping in wild-type *C. elegans*. Next, additional toxicity assays and eventually NPs' effect on pharynx pumping in strains characterized by irregular pumping will be studied as well.

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## **PGA-Protein conjugation of Velaglucerase as novel methodology for increasing the efficiency and efficacy of Gaucher Disease treatment by ERT**

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Enzyme Replacement Therapy (ERT) has revolutionised patient management in Lysosome Storage Disorders (LSD). Gaucher Disease (GD), a disorder caused by mutations in the GBA gene, which encodes for the enzyme Glucocerebrosidase, is the most prevalent LSD. Administration of functional Glucocerebrosidase to GD patients results in a notorious reversion of the visceral manifestations of the disease. Nonetheless, there are important shortcomings in ERT as the inability to cross the Blood-Brain Barrier (BBB), making it ineffective to treat the neurologic manifestations that GD may involve, and poor stability and enzyme activity loss during transportation throughout the bloodstream.

Protein encapsulation has been widely studied in order to overcome the challenges of protein therapeutics in terms of effective and efficient delivery in the site of action. Encapsulation can protect proteins from degradation or inactivation, can carry out a specific delivery and ensure a controlled and sustained release in target. However, the encapsulation process usually has harmful effect in protein stability and/or activity.

Herein we suggest a method for protein modification and coating in Velaglucerase, a recombinant version of Glucocerebrosidase used in GD treatment, in order to overcome the main challenges of ERT. Polymer Masked-Unmasked Protein Therapy (PUMPT) is based on protein conjugation with a biodegradable poly-L-glutamic acid (PGA) polymer that mask protein activity during transportation along the bloodstream, protecting it from harsh environmental conditions. Conjugates stay coated in non-reductive environments such as the bloodstream and are released into highly reductive ones, such as the lysosomes.

The results indicate that Velaglucerase-PGA conjugates successfully reach the lysosome and are able to partially restore Glucocerebrosidase activity in GBA knockout cells, in a similar manner to unconjugated Velaglucerase. Nonetheless, conjugates are much more stable in blood plasma than the unconjugated protein, which rapidly loses its activity. This successful protein conjugation method allow the introduction of surface modifications without modifying the protein itself and thus interfering in its activity, keeping a door opened to specific targeting and BBB crossing.

## **Evaluation of the nano-bio interaction between superparamagnetic iron oxide nanoparticles and *Caenorhabditis elegans***

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*Caenorhabditis elegans* (*C. elegans*) is a 1-mm free-living soil nematode widely used as an assessment platform of nanoparticles. It has an easy experimental manipulation, short life cycle, transparency, large number of offspring and highly conserved genome, which those advantages provide us with a powerful and informative *in vivo* model. We can screen and perform an initial evaluation of nanoparticles (NPs) for biological applications such as therapeutic carriers, biosensors, imaging agents in any chemical lab [1].

Superparamagnetic iron oxide nanoparticles (SPIONs) are promising nanoparticles utilized for medical applications such as drug delivery, cell labelling, hyperthermia therapy due to their high biocompatibility and biodegradability [2]. We expose *C. elegans* to NPs, and we evaluate if the presence of food decreases any possible toxic effect on *C. elegans* exposed to SPIONs in the acute and prolonged condition.

We used a series *C. elegans*'s toxicity endpoints using physical and biochemical techniques in order to study the nano-bio interactions. We found that SPIONs did not affect survival even at the high concentration (500 mg/L). Bio-distribution test showed that SPIONs were homogeneously dispersed in the intestinal lumen, in contrast to previous works. We are also evaluating if SPIONs effects on *C. elegans*' metabolism or if SPIONs give any neurotoxic effects.

I have attended the VI Spanish worm meeting in Valencia in my first year of PhD with a poster. I really enjoyed talking with some colleagues and made some friends. I am delighted to attend the Spanish worm meeting again. I would like to ask for a financial support for my attendance, it could be a great motivation for me to work and cooperate with more people.

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## **Nanocellulose from bacteria as an ocular bandage material**

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Nanocelluloses are cellulosic products with at least one dimension in the nanoscale. Nanocellulose can be extracted from natural sources like wood, cotton or algae but it can also be directly produced by microorganisms. Bacterial nanocellulose (BNC) is a biopolymer naturally synthesized and secreted by *Komagataeibacter xylinus* that forms a 3D-network of pure and interwoven cellulose nanofibres. BNC exhibits attractive properties for biomedical applications such as biocompatibility, great liquid holding capacity, high tensile strength, flexibility and porosity. BNC has already been proposed for diverse biomedical applications, mainly for skin regeneration. Nevertheless, the potential of BNC to treat other damaged tissues, such as the cornea, remains unexploited.

First, structural characterization of BNC films will be presented, followed by detailed cytocompatibility tests of BNC substrates performed in vitro with human dermal fibroblasts. This includes studies about cell attachment, viability, proliferation and morphology of fibroblasts cultured on top of different BNC films. Lastly, our first attempts, performed in close collaboration with clinicians, towards the applicability of BNC in regenerative ophthalmology will be presented. These experiments demonstrate that BNC meets the basic requirements of mechanical resistance to suture, conformability to the eye surface, ex vivo stability and ease of manipulation to be used as a new ocular bandage material. Altogether, our data will point out that BNC is a promising and versatile biomaterial to be used as a vehicle for cell transplantation and/or as a wound healing device to treat ocular surface disorders.

## **Organic thermoelectrics a solar energy harvester**

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This work reports on the ability of organic thermoelectrics to harvest the Sun's energy. The overall efficiency of an organic solar thermoelectric generator will be dependent on the photothermal conversion efficiency and the thermoelectric efficiency of the generator. Common organic thermoelectric materials, such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), poly(3-hexylthiophene (P3HT), and single-walled carbon nanotubes (SWCNTs), are able to convert incident solar radiation into usable heat. With 2 times concentration, a temperature difference of 50 K was able to develop between the illuminated side and the non-illuminated side. For PEDOT:PSS, we observed a photo-conductivity effect as a result of using light as a heat source, however, we observed no noticeable effect on the Seebeck coefficient. We found that only 30%-40% of the generator needs to be illuminated to achieve maximum power and that shorter legs could mean better device performance. Finally, we propose different device architectures based on planar geometries for organic STEGs with and without concentrating mirrors.

## **Raman spectroscopy as a tool for studying the graphene - ionic liquids interaction**

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Understanding the interaction between graphene and ionic liquids is crucial, especially when working with electronic devices based on this bidimensional material, as they may have a wide range of applications. Regardless its importance, little is known about the graphene-liquid interface and its dependence with factors such as the graphene thickness, substrate or the pH of the solution in contact with the material.

In this work, we fabricate CVD graphene electrodes supported on different substrates- of insulating and conductive nature -; which are submerged in ionic solutions of increasing KCl concentration. The monitoring of the influence of the [KCl] on single layer graphene was performed under acidic and basic conditions and with an applied potential or in open circuit configuration.

Raman spectroscopy is a powerful tool for characterizing graphene, and in this work we show also its capability for addressing charge carriers in graphene; since the energy shift of the first order Raman mode of graphene, namely G band, can be related to changes in the graphene Fermi level [1]. Our results reveal a distinctively behavior of graphene when supported on conductive and insulating substrates: while the G band shifts with increasing [KCl] when it is supported on an insulating substrate, no shift is observed when the graphene is placed on a conductive substrate. Results regarding the influence of the pH of the solution reveal opposite shifts of the G band under acidic and basic conditions. Finally, we observed that the amount of induced carriers is directly related to the number of graphene layers.

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## Quasi-adiabatic Nanocalorimetry by Demodulation of Rapidly Oscillating Pulse

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Quasi-adiabatic calorimetry is an adaptation of the pulsed heating traditional method of calorimetry, where a calorimetric cell is heated at high heating rates, typically much faster than the characteristic cooling rates of the cell, to approximate adiabatic conditions and access directly the heat capacity. Reaching extreme heating rates, the sensitivity of the calorimeters could be enhanced permitting to address measurements in small samples. Nevertheless, the method had a no minor limitation that temperature gradients could appear, either between calorimetric cell and sample or even within the sample itself.

At the beginning of the 90s, Leslie Allen and coworker at the university of Illinois developed a new technique that using the quasi-adiabatic method with microfabricated membrane-based calorimeters permitted to measure heat capacity of ultra-thin films samples. The planar configuration of the calorimetric cells and samples permitted to reach rates up to  $10^5 \text{K}\cdot\text{s}^{-1}$  obtaining sensitivities below  $100 \text{pJ}\cdot\text{K}^{-1}\cdot\text{mm}^{-2}$ . To debit the pulse of heat in the calorimeter a high capacitance where instantaneously switched into the electrical resistors of the calorimeter during few milliseconds, providing an almost constant DC current pulse. In this configuration the resulting noise included the addition of the almost complete spectral range, but it could be compensated by the strategy of performing multiple differential measurements enhancing the signal to noise ratio to the Johnson's noise related limit.

In this work, we propose a modification of the method by achieving the short power release (few ms long) in the calorimetric cell injecting alternating currents (or voltage) at much higher frequencies than the characteristic thermal relaxation frequency of the cell. We have used excitation frequencies around  $\sim 100 \text{KHz}$  what effectively is four orders of magnitude higher than the characteristic cooling times of the cell. Under these conditions the calorimetric cell evidences a constant-like power release and the temperature evolution can be measured from the amplitude first harmonic component of the voltage drop in the heater sensor element. Using a fast demodulator (from Zurich Instruments) a single voltage point can be calculated for each excitation period. The resulting measurement presents a signal to noise reduction close to one order of magnitude respect to the previously presented DC method (non-differential), allowing high resolution in single scan experiments.

21.

## **Organic molecular vapour-deposition of glasses under an electric field**

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Glasses with a stability comparable to ordinary glasses aged for thousands of years can be prepared by Physical Vapour Deposition (PVD). One of the key points of PVD is the possibility of tailoring the properties of the deposited molecules with the deposition conditions. Properly setting substrate temperature and growth rate, glasses can show exceptional thermodynamic and kinetic stability. These glasses are the so-called ultrastable, and they are currently gaining attention within the glass community, as their improved packing can yield to outstanding improvements in electronic devices, as it does in OLED efficiency.

An interesting feature of some vapour deposited organic glasses is that molecules can have average spatial orientations that differ from the random distribution of an isotropic glass. The main parameter affecting the molecular orientation seems to be the ratio between the deposition temperature and the glass transition. The possibility of tuning this molecular orientation provides new opportunities to tailor the electrical, thermal, and optical properties of the glassy materials

In this work we propose another strategy to tune the orientation of vapour-deposited molecules of TPD. Applying an electric field, we will create a preferential orientation for this polar molecules when arriving to the substrate. We expect to obtain an enhancement of the stability of their glasses, and an improved electrical conductivity due to the homogeneous orientation.

**Tunable index metamaterials made by bottom-up approaches**

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Despite the exciting electromagnetic properties that negative-index metamaterials exhibit, their implementation in nowadays technology is limited by the traditionally used top-down techniques, which involve costly and low-throughput processes.

As alternative, we present an inexpensive and up scalable route to fabricate double fishnet metamaterials over centimetre-sized areas that relies on the combination of colloidal lithography and metallic electrodeposition. Our design is based on a hexagonally ordered monolayer of polystyrene beads used as template for the infiltration of two symmetric gold layers separated by an air gap.

The obtained structures have been characterized by vis-NIR microspectroscopy, exhibiting extinction resonances in the near-infrared range. The good agreement between the optical measurements and the finite-difference time-domain (FDTD) simulations attests the success of our fabrication process.

The effective optical properties, retrieved from the calculations by the homogenization method, demonstrate that we are experimentally able to tailor the refractive index from positive to negative and zero values by the proper choice of the particles diameter and the gap width between the metallic layers. In particular, negative metamaterials with a refractive index of -1 in the near-infrared and working over a 100 nm wide spectral range have been successfully fabricated.

Our results open the door to a new approach for the low-cost fabrication of negative-index metamaterials.

## Low-cost point-of-care biosensor device for on-site tuberculosis diagnosis in developing countries

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Tuberculosis (TB), an infectious disease caused by *Mycobacterium tuberculosis*, is considered the leading global cause of death from a single infectious agent. Registered incidence rates are scarce, especially in low-resource countries, due to the disadvantages of current diagnostic methods, which are slow, expensive, insufficiently accurate, time consuming, not portable or require trained technicians. For that reason, since several years ago, a major effort is directed to develop a low-cost point-of-care (PoC) diagnostics platform able to deliver a prompt response in order to reduce TB deaths. We have fully developed a novel PoC biosensor platform for fast TB detection in the frame of the European FP7 Pocket Project. The new PoC biosensor allows the detection of active TB directly in human urine, taking advantage of the high sensitivity offered by the evanescent wave optical sensors employed. The photonic sensor is based on a highly sensitive Mach-Zehnder Interferometer transducer with an on-chip spectral filter and is incorporated in a disposable microfluidic cartridge. The required elements for light coupling and optical readout are integrated in a prototype instrument, which allows real-time monitoring and data processing.

To detect active *M. tuberculosis* we focus in several biomarkers present in the urine of TB patients, including lipoarabinomannan (LAM), early secretory antigenic target (ESAT-6), culture filtrate antigen (CFP-10) and immunogenic protein (MPT64), respectively.

First results have been achieved for LAM biomarker, a lipopolysaccharide found in the mycobacterium cell wall. For the detection, the sensor chip surface was functionalized with high-quality and selective monoclonal antibodies against LAM. After the optimization of several parameters, a limit of detection of 475 pg/mL was achieved using a direct immunoassay. The analysis was performed in undiluted urine in less than 15 minutes. In addition, the results were validated by using 20 clinical samples from TB patients from Tanzania and healthy donors, showing an excellent correlation between the results from the PoC biosensor and those obtained with standard techniques.

After these promising results for one biomarker and in order to take the advantage of the PoC design for the simultaneous detection of a panel of six different biomarkers

in the same patient's sample, all the optimizations for the evaluation of the other three biomarkers, mentioned above, is in progress.  
24.

## **Photovoltaic Effects of Insulating Layer on LuMnO<sub>3</sub> Ferroelectric Single Crystal**

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Photovoltaics as the environmentally friendly energy source have been extensively researched, however, large scale application requires low cost and high efficiency. A plausible way to enhance performance could be using materials with an internal spontaneous electric field extending all over the material, by which photocharges can be driven towards the electrodes, rather than in a narrow layer as the conventional PN junction does. To discover more efficient photovoltaics, light should be efficiently absorbed, which implies materials with a relatively narrow bandgap are better for absorbing all visible spectra. In addition, materials should be more robust by nature than current materials. Therefore, oxides come as a good choice to explore.

As ferroelectric photovoltaics with low bandgaps, hexagonal rare-earth Manganites have drawn much attention owing to their long-term stability, environmental safety, anomalously high photovoltages, relatively high and switchable photocurrents. However, in ferroelectric semiconductors with ideal contacts, the polarization charge would be fully screened by metal electrodes and no depolarization field would exist. By adding an Insulating Layer (IL) between the ferroelectrics and electrodes, the depolarization field exists and can be adjusted then affects the photoresponse of ferroelectrics.

Herein, we present a series of h-LuMnO<sub>3</sub> ( $E_{\text{gap}} \sim 1.5$  eV [1]) single crystals (thickness  $\sim 200$   $\mu\text{m}$ ) sandwiched between Pt electrodes with and without AlO<sub>x</sub> of different thicknesses as an IL. According to the hysteresis and photovoltaic IV measurements, without AlO<sub>x</sub>, there show ferroelectricity and photovoltaic response. Besides, the illuminated interface rays the photoresponse and the polarization direction modifies the short circuit current  $I_{\text{sc}}$ , but there is no big contrast on photoresponse between different polarization direction. While with AlO<sub>x</sub>, there show contrasts between different polarization direction, and the  $I_{\text{sc}}$  (up to  $\sim 6.99$  mA/cm<sup>2</sup> when the IL layer is  $\sim 56$  nm.) and the maximum power  $P_{\text{m}}$  increase exponentially first than decrease with the thickness of AlO<sub>x</sub> increases. Thus, adjusting the IL may be a useful way to improve the efficiency of photoferroelectrics.

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25.

## **Physical Characterization of Filamentary Structures in TiN/Ti/HfO<sub>2</sub>/W Memristor Devices**

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Memristors based on the resistive switching (RS) phenomenon are promising devices for many future applications, such as non-volatile memories and electronic synapses in neuromorphic circuits. These devices can be switched between a high (HRS) and a low (LRS) resistance state by performing RESET and SET operations, respectively. The RS devices are mainly based on metal-insulator-metal (MIM) structures. The physical mechanism responsible for the RS behavior is the formation and partial disruption of a nanometer-size conductive filament (CF) in the insulating layer, connecting the top (TE) and bottom (BE) electrodes. These CFs are composed of structural and chemical defects. To optimize the devices performance, it is crucial to obtain a better understanding of the RS physical mechanism.

In this experimental work, a new methodology is presented to characterize, locate and identify the filamentary paths in HfO<sub>x</sub>-based RS devices. The proposed technique includes the following steps:

1) RS devices with TiN/Ti/HfO<sub>2</sub>/W structures were fabricated on Si-n<sup>++</sup> wafers. The 10nm-thick HfO<sub>2</sub> layer was deposited by atomic layer deposition.

2) The devices were electrically characterized. Voltage was applied to the TE while the BE was grounded. Initially, the CF “forming” process was performed to the fresh device applying a positive voltage ramp and limiting the current in order to prevent dielectric hard breakdown. Next, 20 consecutive RS sweep cycles were performed.

The devices were electrically driven to three different states: LRS, HRS and a degraded state.

3) The TiN/Ti TE was removed by chemical etching.

4) Finally, the devices were inspected by SEM, EDX and AFM techniques. In all the electrically measured devices, a plated-shaped structure was revealed due to the etching of the BE with radial symmetry. The reactants reached the BE through the filamentary path that was located at the center of these “microplates”. The observed filamentary structures were: a hole (devices in LRS), an almost sealed hole (devices in HRS) and a big sponge-like structure (electrically degraded devices). In pristine devices, neither microplates nor filamentary structures were found.

The results show that this new characterization methodology allows to reveal the position of the CF in HfO<sub>x</sub>-based devices. In addition, the analysis of the results has

highlighted the correlation between the device electrical degradation, the resistance state and the physical nature of the filamentary path.

26.

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

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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<sub>2</sub> 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<sub>2</sub> 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 synergy between the redox and the conducting species giving rise to enhanced currents and lower overpotentials. For example, the addition of both carbon nanotubes and IrOx in aqueous alkaline electrolyte results in that mentioned synergy leading in a more favorable OER, whereas no large effect compared to the blank electrolyte is seen when only adding neither carbon nanotubes nor IrOx. The relevant parameters and hypothesis for a mechanism will be discussed.

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27.

## **Design optimization of low cost, highly efficient aqueous Zinc-iodide flow battery**

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Redox flow battery (RFB) is getting vast attraction for storing intermittent energy from renewable sources such as solar and wind energy due to its design flexibility in decoupling energy and power. In spite of long cycle life, the most widely investigated all vanadium redox-flow batteries (VRFB) are limited by low energy density and insufficient resource of vanadium. Upscaling the energy density of the RFBs can be achieved by increasing the number of electron involved in the half-cell reactions. Zinc-iodide flow battery (ZIFB) is attractive among current flow batteries due to its several advantages over VRFB, such as two-electron transfer in the half-cell reactions which leads to enhanced energy density; zinc is a low cost, earth abundant material; use of acid-free electrolytes. In 2015, Li et al. (Nature comm., 2015, 6, 6303), firstly reported ZIFB with high energy density based on aqueous zinc iodide (ZnI<sub>2</sub>) as electrolyte. However, deposition of iodine (I<sub>2</sub>) in the catholyte during cycling significantly decrease the stability of the electrolytes. Highly soluble potassium iodide (KI) as electrolyte additive can mitigate the problem of solid iodine (I<sub>2</sub>) deposition. On the other hand, inhomogeneous growth of Zn dendrite on the surface of the negative electrode can lead the cell to improper discharge. Modification in the full-cell design gives a way out to resolve this issue and improve the overall performance of the cell. By using pre-treated and/ or different carbon electrodes in order to provide more active sites for the redox reactions and to increase electrical conductivity; assembling with different cell configurations to protect the membrane from direct contact with deposited products, could be possible to eliminate the effect of non-uniform dendrite growth on the cell cycling performance and achieve high coulombic efficiency of 96% and energy efficiency of 81%. Overall, ZIFB, having features like higher capacity, higher efficiency among other aqueous flow batteries, and less corrosive electrolytes are promising next generation aqueous flow batteries, suitable for the integration with Photovoltaic systems to make future 'Photobatteries'.

28.

## **Impact of substitutional groups in the interfacial doping of organic semiconductors**

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Derivatives of BTBT([1]benzothieno[3,2- b][1]benzothiophene) are some of the most promising organic semiconductors for organic field effect transistors(OFETs) due to its high intrinsic charge carrier mobility [1-2]. One critical issue in BTBT-based OFETs is the large injection barrier at gold electrodes. Contact doping (or surface transfer doping), where a thin injection layer is inserted between the organic film and electrode, has been successfully employed as a strategy to reduce the contact resistance in p-type organic field effect transistors(OFETs)[3,4]. The concept of contact doping relies on the charge transfer between OSC and dopant molecules across their interface. Still very little is known about how the doping efficiency depends on the specific structural and electronic properties of the interface. To address this issue, in this work, we focus on a comparative study of two BTBT derivatives, C8-BTBT and DPh-BTBT, substituted with alkyl chains and phenyl groups, respectively(Figure 1a).

As molecular p-dopant, we have chosen the fluorinated fullerene, C60F48 which shows low volatility, bulkier shape and higher thermal stability than already established dopants[5]. In this work, we investigate the structure, growth, thermal stability and electronic properties. We employ KPFM to follow the molecular organization of C60F48 at the interface with increasing coverage and to quantify local changes in work function. The evolution of the crystallinity has been investigated by grazing Incidence Xray Diffraction(GIXD). To have a comprehensive picture, Photoelectron Spectroscopy (XPS and UPS) measurements have been performed as well to know more about the correlation between the structural and electronic properties at the diverse organic interfaces. The feasibility of the approach has been preliminarily tested in OFETs.

