



Virtual European School on Molecular Nanoscience



Videoconference schedule

Wednesday June 3rd

9:30-10:30 Welcome & Seminar: Invited lectures discussion

Discussion of their lectures with **Toribio Fernández**, **Nazario Martín** & **Josep Puigmartí**

Toribio FERNÁNDEZ OTERO- Universidad Politécnica de Cartagena

How we can replicate and quantify biological functions?

Nazario MARTÍN - Universidad Complutense de Madrid

Bottom-up Synthesis of (Chiral) Nanographenes

Josep PUIGMARTÍ- ETH Zurich (CH)

Micro- and nano-fluidic technologies for chemistry and materials science

10:30-11:00 Break

11:00-12:30 Students oral communications

Mirela ENCHEVA - Universidad Miguel Hernández

Toxicity and cellular internalization of water-soluble imidazolium- and pyridinium-containing Perylenediimide Salts

Modesto GONZÁLEZ-RODRÍGUEZ – Universidad de La Laguna

Hydrogen production by water splitting technique using (g-C₃N₄)_x(CdS)_{1-x} as photocatalyst

Clara PÉREZ GONZÁLEZ- Universidad de Valladolid

Design and development of a potentiometric e-tongue with nanomaterials for the dairy industry

Alfonso GONZÁLEZ – Universidad de Valladolid

Langmuir-Blodgett Biosensors based on Substituted Metallic Phthalocyanines and the Influence of the Enzyme-Mediator Interaction in the Electrochemical Detection of Galactose

Jesús CASES - ICMol- Universitat de València

Encapsulation of proteins in MOFs by biomineralization

David HERRERO - Universidad Miguel Hernández

Silicon Phtalocyanine-Based Surface Functionalized Metal-Organic Frameworks as Active Materials in Optical Cavities

12:30-13:00 Final discussion

Thursday June 4th

9:30-11:00 Seminar: Invited lectures discussion

Discussion of their lectures with **Andrés Castellanos, Alicia Forment, J Ignacio Pacual, Diego Peña & Francisco Rivadulla**

Andrés CASTELLANOS - Instituto de Ciencia de los Materiales de Madrid-CSIC

[*Tutorial on devices based on 2d materials*](#)

Alicia FORMENT- ICMol- Universitat de València

[*Overview about MoS₂ exfoliation & functionalization in solution*](#)

J Ignacio PASCUAL- CIC NanoGUNE

[*\$\Pi\$ -magnetism in graphene nanostructures*](#)

Diego PEÑA- CIQUS-Universidad de Santiago de Compostela

[*Combining Organic Synthesis with Surface Science: from Insoluble Molecules to Graphene Materials*](#)

Francisco RIVADULLA - CIQUS-Universidad de Santiago de Compostela

[*Local manipulation of oxygen ions in functional oxides*](#)

11:00-11:20 Break

11:20-12:50 Students oral communications

Tamara DE ARA – Universidad de Alicante

STM Study on Dithia[7]Helicenes and Organic Solvents on Au(111) Surface

Yelko DEL CASTILLO HERNÁNDEZ- Universidad de Alicante

Quantum transport in graphene nanocontacts

Marta ALCARAZ MEGÍAS- ICMol- Universitat de València

Synthesis and Characterization of Few-Layer Hexagonal Antimonene Nanosheets via Colloidal Approach

Marta VEGAS GARCÍA - ICMol- Universitat de València

Comparison between top-down and bottom-up synthetic approaches in production of antimonene for both cell internalization and cell viability

María CASTILLO ORENES - Universidad Miguel Hernández

Phtalocyanines-Spirofluorene Systems as Hole Transporting Materials in Perovskite Solar Cells

Ana M. IGUAL MUÑOZ- ICMol- Universitat de València

Wide-Bandgap Inorganic Perovskite synthesized through sublimation methods for solar cell applications

Abhyuday PALIWAL - ICMol- Universitat de València

Semi-transparent metal thin-film electrode-based perovskite solar cells

12:50-13:00 Final discussion

Friday June 5th

9:30-10:30 Seminar: Invited lectures discussion

Discussion of their lectures with **Núria Aliaga & Eliseo Ruiz**

Núria ALIAGA ALCALDE- Institut de Ciència de Materials de Barcelona-CSIC

[*Overview of the use of Curcuminoids in Single-Molecule Electron Transport Studies*](#)

Eliseo RUIZ - Universitat de Barcelona

[*Improving Slow Spin Relaxation Properties by Encapsulation*](#)

10:30-11:00 Break

11:00-12:30 Students oral communications

Pedro ESQUERDO TEROL-Universidad de Castilla La Mancha

Hole Trapping Dynamics in Covellite CuS Nanodisks

Rafael DELGADO-GARCÍA- Universidad de Castilla La Mancha

Shape-related effects on a single ferromagnetic nanoparticle: A micromagnetic approach

Ruben TURO-CORTÉS - ICMol- Universitat de València

One- vs two-step Spin Crossover modulation through host-guest chemistry in amino-functionalized 2D Hofmann-type coordination polymers

Cristina GARCÍA PÉREZ– Universidad Autónoma de Madrid

Hybrid Superconducting Nanowires Single-Photon Detectors

Raquel NARANJO ALCÁZAR - ICMUV- Universitat de València

Selective Transport Metal Oxides

12:30-13:00 Final discussion and conclusions

Following can be found the Oral Communications abstracts in alphabetical order.

Synthesis and Characterization of Few-Layer Hexagonal Antimonene Nanosheets via Colloidal Approach

Marta Alcaraz,¹ Roger Sanchis-Gual,¹ Jose A. Carrasco,¹ Mhamed Assebban,^{1,2} Michael Fickert,^{1,2} Gonzalo Abellán.^{1,2}

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Two-dimensional (2D) pnictogen materials (P, As, Sb and Bi) have attracted increasing attention in the last years due to their outstanding physical properties and their potential applications in optoelectronics, sensors, energy storage and conversion or organic catalysis, to name a few.[1,2] Nevertheless, the application of BP in both electronic and optoelectronic devices is limited by its instability under ambient conditions. In contrast to BP, antimonene was predicted through first-principle calculations to be highly stable, exhibiting extraordinary properties[3] and has recently been isolated by micromechanical exfoliation and liquid phase exfoliation (top-down approaches).[4] However, the synthesis of high-quality layers of antimonene in larger quantities can only be addressed via a bottom-up approach. In this work, we prepare few-layer antimonene nanosheets using a colloidal chemistry route[5], which allows the synthesis of better quality nanosheets from the points of view of surface oxidation, morphology and size. These nanosheets were characterized with electron microscopy, atomic force microscopy, Raman spectroscopy, and X-ray powder diffraction, among others. In addition, with the aim of achieving thinner hexagonal nanosheets with greater lateral dimensions, we have carried out an exhaustive study of the influence of different reaction parameters. Overall, the results obtained from this study provide an in-deep understanding of the final material and allow the optimization of the experimental conditions paving the way for the development of electronic applications.

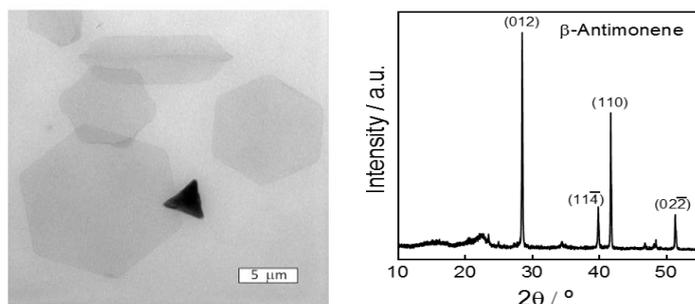


Figure 1: Transmission electron microscopy image (left) and X-ray powder diffraction (right) of hexagonal antimonene nanosheets synthesized using a colloidal chemistry approach.

[1] Lloret, V., Rivero-Crespo, M. Á., Vidal-Moya, J. A., Wild, S., Doménech-Carbó, A., Heller, B. S., Shin, S., Steinrück, H. P., Maier, F., Hauke, F., Varela, M., Hirsch, A., Leyva-Pérez, A., Abellán, G. *Nat. Commun* **2019**, 10, 509.

[2] Ares, P., Palacios, J. J., Abellán, G., Gómez-Herrero, J., Zamora, F. *Adv. Mater* **2018**, 30, 1703771.

[3] Abellán, G., Ares, P., Wild, S., Nuin, E., Neiss, C., Miguel, D.R.-S., Segovia, P., Gibaja, C., Michel, E.G., Görling, A., Hauke, F., Gómez-Herrero, J., Hirsch, A., Zamora, F. *Angew. Chem. Int. Ed* **2017**, 56, 14389.

[4] Gibaja, C., Rodríguez-San-Miguel, D., Ares, P., Gómez-Herrero, J., Varela, M., Gillen, R., Maultzsch, J., Hauke, F., Hirsch, A., Abellán, G., Zamora, F. *Angew. Chem. Int. Ed* **2016**, 55, 14345.

[5] Peng, L., Ye, S., Song, J., Qu, J. *Angew. Chem. Int. Ed* **2019**, 58, 9891.

Encapsulation of proteins in MOFs by biomineralization

Jesús Cases, M. Giménez-Marqués¹

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A critical challenge in biotechnology is the preservation of biomolecule activity to ensure their use in pharmaceuticals, chemical processing and biostorage. A plausible solution widely explored consists on using a protective coat for biomolecules enhancing their robustness and ensuring biological activity. In this sense, Metal-Organic Frameworks (MOFs) have been recently explored, resulting excellent candidates as a protective coat for biomolecules due to their unique properties (1). These hybrid crystalline porous materials, constituted by both organic and inorganic components, are thermally and chemically stable, and can be synthesized under mild biocompatible conditions.

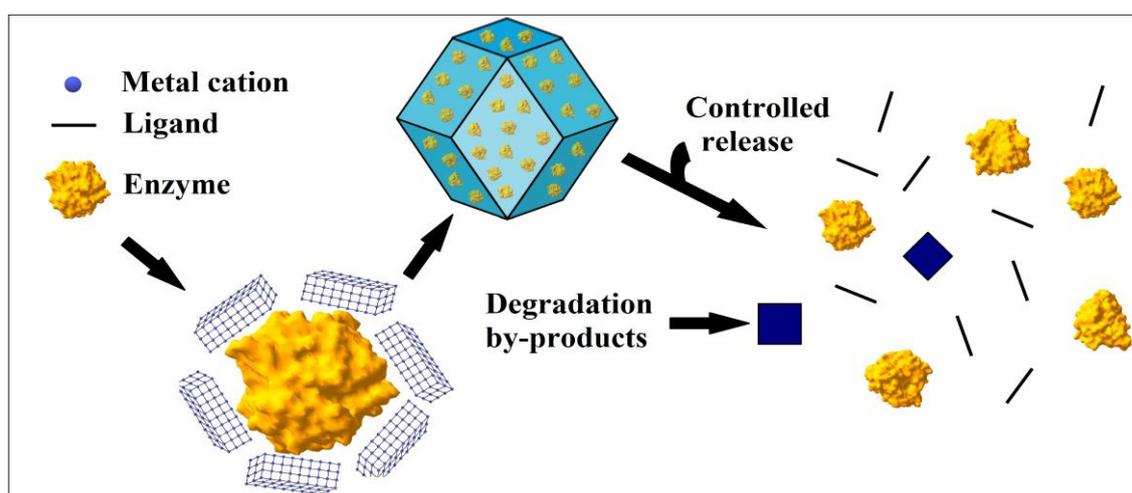
Among the different strategies reported to encapsulate proteins (enzymes) in a MOF, biomimetic mineralization is raised as the most appropriate (2). In this process, the protein can interact with the precursors of the MOF during the synthesis, leading to the formation of protective MOF coatings under desired physiological conditions. This rapid, low-cost process gives rise to new possibilities for the exploitation of biomacromolecules, significantly increasing their potential in applications where enhanced thermal stability, tolerance to organic solvents or extended shelf-lifetime is required, such as industrial catalysis and biopharmaceutical delivery.

Despite the wide variety of potential MOF that can be synthesized in biocompatible conditions, only zeolitic imidazolate frameworks (ZIFs) have been primarily studied, likely due to their exceptional chemical and thermal stability and negligible cytotoxicity. These ZIFs can be grown under mild biocompatible conditions thus preserving enzymatic activity. The encapsulated proteins can be released simply by a pH change within a physiological environment.

Herein we present the encapsulation by biomineralization using a different biocompatible MOF, the mesoporous trimesate iron-based MIL-100 material.

References:

- (1) K. Liang, C. J. Coghlan, S. G. Bell, C. Doonan and P. Falcaro. Enzyme encapsulation in zeolitic imidazolate frameworks: a comparison between controlled co-precipitation and biomimetic mineralization. *Chem. Commun.*, **52**, 473—476 (2016). <https://doi.org/10.1039/C5CC07577G>
- (2) Liang, K., Ricco, R., Doherty, C. et al. Biomimetic mineralization of metal-organic frameworks as protective coatings for biomacromolecules. *Nat. Commun.* **6**, 7240 (2015). <https://doi.org/10.1038/ncomms8240>



Phthalocyanines-Spirofluorene Systems as Hole Transporting Materials in Perovskite Solar Cells.

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Organic chemistry is making great advances in the design and synthesis of molecular systems that can imitate photosynthetic processes, a new alternative to obtain energy in a more respectful way with the environment.^[1] In order to attend this necessity, new solar devices based on the photoinduced electron transfer are being carried out like the Perovskite Solar Cells (PSCs) that are one of the "hotspots" in research due to the high solar efficiencies achieved that one day can maybe substitute the silicon solar cells.^[2] The best efficiencies in PSCs have been obtained by the application of Hole Transporting Materials (HTMs) that act as p-dopant molecules due to their high hole mobility.^[3]

Phthalocyanines (Pc) are one of the most promising molecules as HTMs due to its easy synthesis and processability, great stability, intensive absorption and its 18 π -electrons that can be easily donated as well as they can improve the stability of the active layer of perovskite.^[4] The advantages of use of different metal phthalocyanines (MPcs) as HTMs has been already described and recently the possibility of apply Pc dimers instead of monomers can suppose an advance to achieve highly efficient PSCs.^[5]

The aim of this work is to synthesize and characterize zinc-phthalocyanine dimers directly connected (**Figure 1a**) or through an ethynyl linker (**Figure 1b.**) to a spirobifluorene, in order to act as HTMs in PSCs and to compare how the different nature of the bridges influences the performance of the devices.

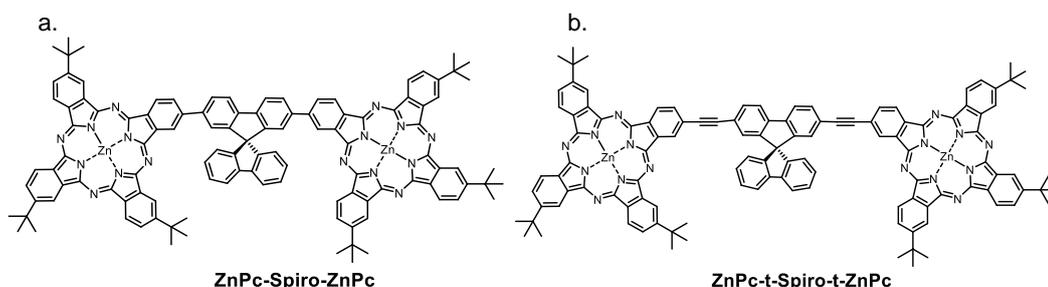


Figure 1. Chemical structure of a. ZnPc-Spiro-ZnPc structure b. ZnPc-t-Spiro-t-ZnPc

[1] V. Balzani, A. Credi, M. Venturi. *ChemSusChem*, **2008**, *1*, 26–58.

[2] M. Saliba, J.P. Correa-Baena, C. M. Wolff, M. Stollerfoht, N. Phung, S. Albrecht, A. Abate. *Chem. Mater.*, **2018**, *30*, 13, 4193–4201.

[3] M. Urbani, G. de la Torre, M. K. Nazeeruddin, T. Torres. *Chem. Soc. Rev.* **2019**, *48*, 2738-2766.

[4] M. Saliba, J.P. Correa-Baena, M. Grätzel, A. Hagfeldt A. Abate, *Angew. Chem. Int. Ed.*, **2018**; *57*, 2554–2569.

[5] a) D. Molina, M.A. Ruiz-Preciado, F. Sadegh, M.J. Álvaro-Martins, M. Grätzel, A. Hagfeldt, Á. Sastre-Santos. *J. Porphyrins Phthalocyanines*, **2019**, *23*, 546–553. b) D. Molina, M. A. Ruiz-Preciado, B. Carlsen, F. T. Eickemeyer, B. Yang, N. Flores-Díaz, M. J. Álvaro-Martins, K. Nonomura, A. Hagfeldt, Á. Sastre-Santos, *ChemPhotoChem* **2020**, in press; doi: 10.1002/cptc.201900245.

STM Study on Dithia[7]Helicenes and Organic Solvents on Au(111) Surface

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For this work, a Scanning Tunneling Microscope (STM) [1] is used to study a solution of dithia[7]helicenes in benzene and three different organic solvents. Two different dithia[7]helicene molecules ([7]DTH) were synthesized with sulfur atoms integrated in different locations. We can distinguish two topologies in function of the sulfur position, known as *exo* and *endo* (Figure 1). Thus, we deposited and evaporated the solution on Au(111) surfaces and then, we observed how they are distributed due to the interactions of the sulfur as a link group with the gold atoms. It was possible to image different binding configurations and arrangement of the [7]DTH over the surface. Also, single molecules were clearly identified and characterized. As we were working with benzene, a study on different solvents were carried out. This was supported by the distinction of the solvent molecules in the topographic images when the solution was diluted enough. Thus, we selected benzene, cyclohexane and toluene as three common solvents to perform a STM study and compare their contributions. Also, we perform STM-based break junction (BJ) measurements for the solvent molecules in order to characterize their most-likely conductance values. All these experiments were carried out under ambient conditions.

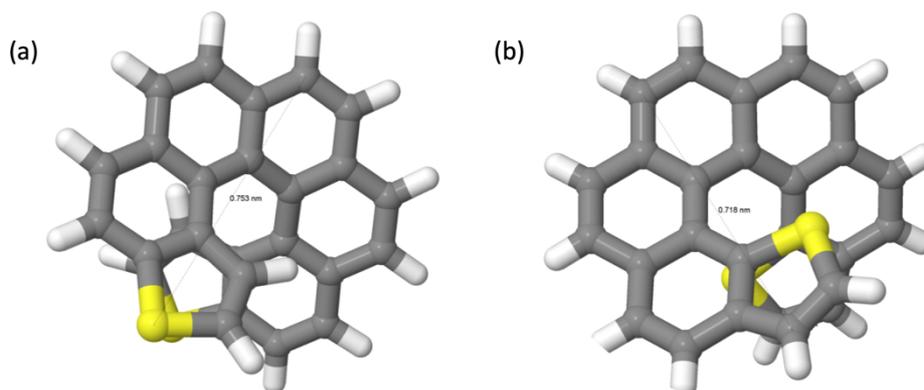


Figure 1 – Chemical structure of the dithiahelicenes considered in this work: (a) *exo*-dithia[7]helicene and (b) *endo*-dithia[7]helicene.

[1] G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Surface Studies by Scanning Tunneling Microscopy, *Phys. Rev. Lett.* **1982**, 49, 57

Quantum transport in graphene nanocontacts

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In this work, we present a theoretical study about the electronic transport between two graphene nanoribbons connected through an atomic-sized contact. We have study in detail how the shape and size of the constriction contributes to the conductance. All the computational calculations are performed using tight-binding Hamiltonians and the python package Kwant [1]. As a result of this study, in contrast with metallic atomic-sized contacts, we have observed that graphene nanocontacts do not conduct.

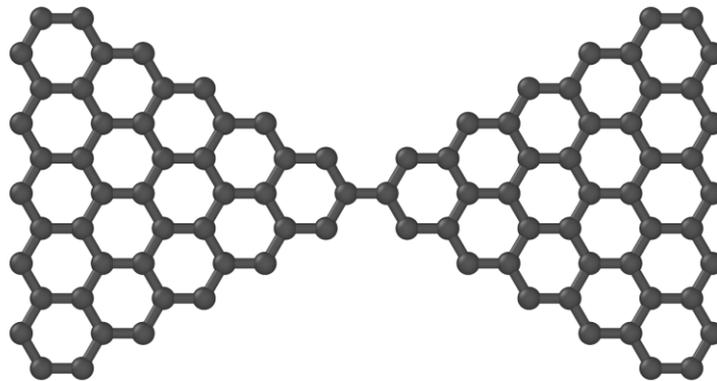


Figure 1. Mono-atomic contact between two triangulenes.

[1] C. W. Groth, M. Wimmer, A. R. Akhmerov, X. Waintal, New J. Phys. 2014 16, 063065.

Shape-related effects on a single ferromagnetic nanoparticle: A micromagnetic approach

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Micromagnetic simulations have been carried out using software mumax³ [1] and Nmag [2], which use finite-difference and finite-element methods respectively to solve the Landau-Lifshitz-Gilbert Equation [Equation 1] regarding the precessional motion of magnetization on a ferromagnetic material exposed to an external magnetic field.

$$\frac{d\mathbf{M}}{dt} = -\gamma' \mathbf{M} \times \mathbf{H}_{\text{eff}} - \lambda \mathbf{M} \times (\mathbf{M} \times \mathbf{H}_{\text{eff}})$$

Equation 1. Landau-Lifshitz-Gilbert Equation [3].

M: magnetization, t: time, H_{eff}: effective magnetic field.

γ': precessional term (depends on a damping parameter, λ).

Hysteresis loops of nanoparticulate ferromagnetic systems have been simulated along several directions such as (100), (110) and (211). The results show that finite-difference method, which implies building up a spherical or ellipsoidal nanoparticle out of cubes, leads to magnetostatic anisotropy effects especially noticeable in null magnetocrystalline anisotropy systems. In these simulations the demagnetizing factor plays a key role, changing drastically the behaviour of the magnetic moments inherent to the simulated nanoparticle depending on the direction of application of the external field, size of the mesh used to simulate [Figure 1], or Anti-Aliasing [Figure 2].

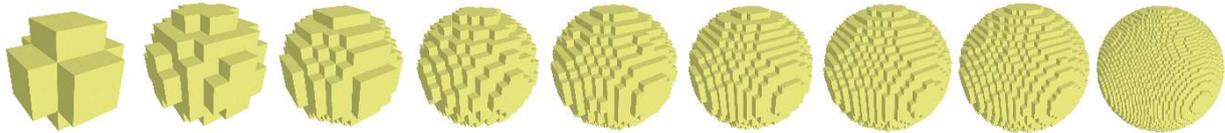


Figure 1. Meshes used for finite-difference simulations in mumax³. From left to right: 4x4x4, 8x8x8, 12x12x12, 16x16x16, 20x20x20, 24x24x24, 28x28x28, 32x32x32, 64x64x64.

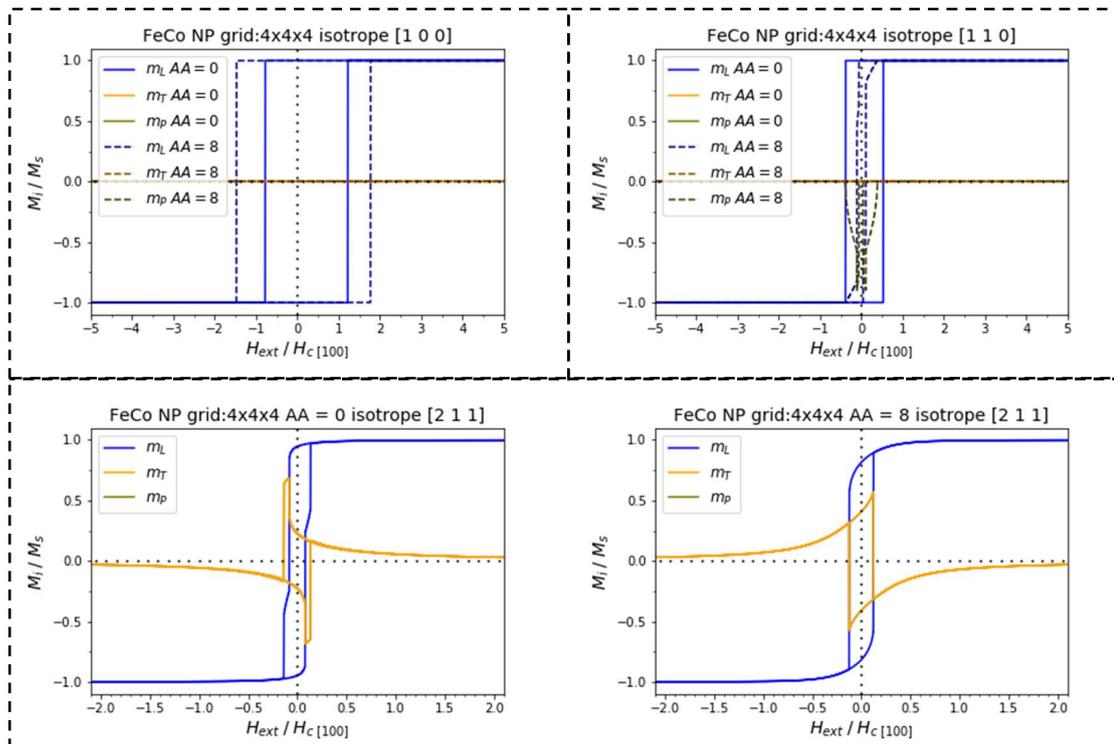


Figure 2. Effect of the direction of the applied field on the hysteresis loops obtained for pseudo-spherical meshes generated in mumax³. Drastically different hysteresis loops are obtained in directions (110) and (211) as a result of geometry and Anti-Aliasing of the simulation mesh.

- [1] Vansteenkiste, A., et al. The design and verification of MuMax3 *AIP Advances* **2014**, 4, 107133
- [2] Fangohr, H., et. al. Nmag micromagnetic simulation tool: software engineering lessons learned *SE4Science '16: Proceedings of the International Workshop on Software Engineering for Science* **2016**, 5, 1-7
- [3] Aharoni, A. Introduction to the Theory of Ferromagnetism *Clarendon Press* **1996** ISBN 978-0-19-851791-7

Toxicity and cellular internalization of water-soluble imidazolium- and pyridinium-containing Perylenediimide Salts

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Photodynamic therapy (PDT) is a photochemical non-invasive treatment based on singlet oxygen (1O_2) generation to face different diseases such as cancer [1,2]. This technique is based on the use of organic photosensitizers [3,4], such as perylenediimides (PDIs), which are a family of fluorophores with high thermal and photochemical stabilities and high fluorescence quantum yields in organic solvents [5]. One of the main challenges in PDI research for PDT is its functionalization in order to gain water solubility. In this work, we have synthesized two water-soluble PDIs based on imidazolium (PDI-1) and pyridinium (PDI-2) salts (Figure 1). Moreover, we have tested them for biocompatibility with fibroblasts in order to optimize the PDI concentration where no toxicity is observed, and to study the internalization of these compounds.

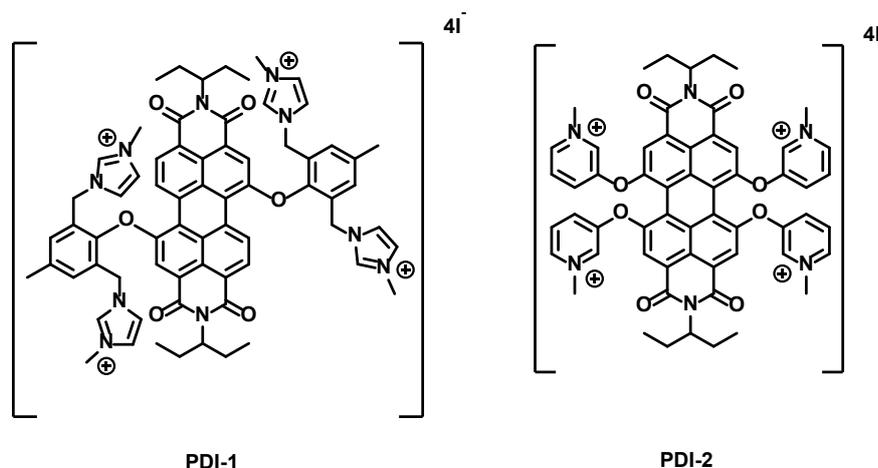


Figure 1.- Structure of PDI-1 and PDI-2

[1] L Benov. *Med. Princ. Pract.* **2015**, *24*, 14-28.

[2] L. R. Braathen, C. A Morton, N. Basset-Seguin, R. Bissonnett, M. J Gerritsen, Y. Gilaberte, P, Calzavara-Pinton, A. Sidoroff, H. C Wulf, R. M. Szeimies. *J. Eur. Acad. Dermatol. Venereol.* **2012**, *26*, 1063-1066.

[3] B. M. Amos-Tautua, S. P. Songca, O. S. Oluwafemi. *Molecules* **2019**, *24*, 2456 1-28.

[4] A. B. De Oliveira, T. M. Ferrisse, R. S Marqués, S. R. de Annunzio, F. L. Brighenti, C. R. Fontana. *Int. J. Mol. Sci* **2019**, *20*, 3585 1-16.

[5] A. Nowak-Król, F. Würthner. *Org. Chem. Front.* **2019**, *6*, 1272-1318.

Hole Trapping Dynamics in Covellite CuS Nanodisks

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In the last decades plasmonic materials have become one of the most investigated in the field of material science. More specifically, copper chalcogenides, $\text{Cu}_{(2-x)}\text{S}$, nanocrystals have attracted attention due to their potential application in photonic devices.^[1] Here, we present the results of time-resolved transient absorption studies on the generation, evolution and trapping mechanism of hot holes in solid state hexagonal covellite (CuS) nanodisks (Figure 1). This is an important feature given the crucial role that trapped holes could play in hetero-interface hole transfer processes such as plasmon-induced transient carrier transfer (PITCT) for example^[2], a promising mechanism that could lead to the development of highly efficient solar cells. We carried out a femtosecond transient absorption (TA) study exciting the plasmonic band of the CuS nanodisks with a 1000 nm pulse and compared the behaviour with the results following excitation at 360 nm, where the system is excited over the bandgap of the covellite. For both pump wavelengths, we found the existence of two clearly related species associated with ultrafast trapping of the holes to shallow and deep trap states, followed by slow relaxation. This could indicate a dominant conductive behaviour of the photogenerated holes. We performed a systematic study on the effect of the excitation pump fluence on the hot hole dynamics to elucidate the possible second order effect that other semiconductor NP present^[3], not finding any determinant evidence of such effects. Finally, we compare two samples synthesized via two different methods to determine precursors and ligand effects on the charge carrier dynamics.

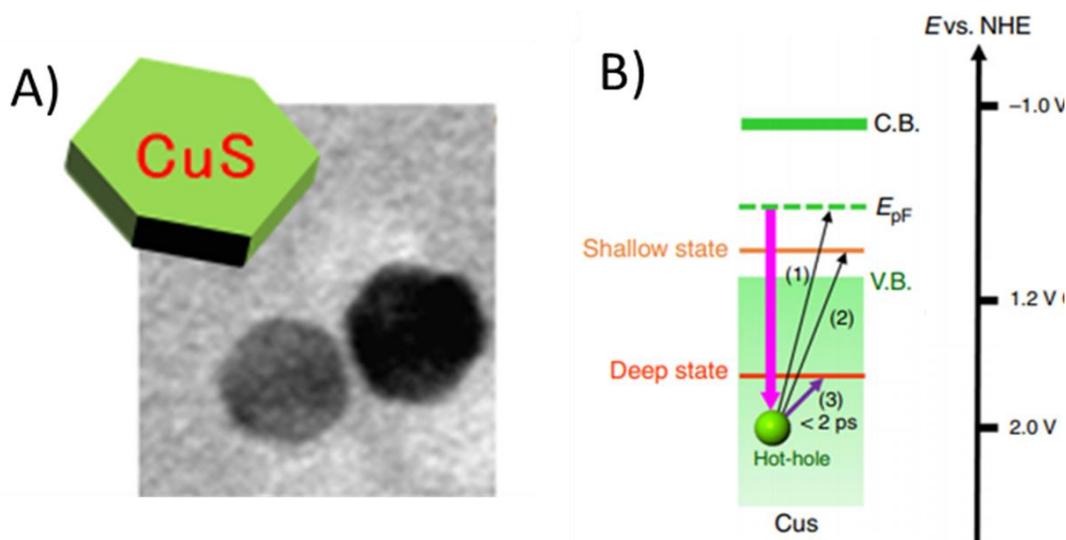


Figure 1: A) TEM image of two covellite hexagonal nanocrystals of approximately 16.3 nm width 6 nm thick. B) Schematic representation of the energy levels and proposed processes in covellite nanodisks following excitation at 1000 nm. (1), (2) and (3) correspond to decay via hole-hole and phonon-hole scattering, ultrafast hole trapping to shallow or deep trapping states, respectively^[2].

Acknowledgments: This work was supported by the International Collaborative Research Program of the Institute for Chemical Research, Kyoto University, Japan, grant # 2019-49, and MINECO (Spain, MAT2017-86532-R).

References:

- [1] E. Petryayeva, U. J. Krull, *Analytica Chimica Acta* **2011**, 706, 8-24.
- [2] Z. Lian, M. Sakamoto, H. Matsunaga, J. J. M. Veqizo, A. Yamakata, M. Haruta, H. Kurata, W. Ota, T. Sato, T. Teranishi, *Nature Communications* **2018**, 9, 2314.
- [3] K. Schwarzburg, F. Willig, *Applied Physics Letters* **1991**, 58, 2520-2522.

Hybrid Superconducting Nanowires Single-Photon Detectors

Cristina García-Pérez¹, Víctor Marzoa¹, Marina C. De Ory^{1,2}, María Acebrón¹, Julia García-Pérez¹, María Teresa Magaz^{1,2}, Fernando J Urbanos¹, Alicia Gómez², Ramón Bernardo-Gavito¹, Daniel Granados¹.

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Abstract

Superconducting nanowire single-photon detectors (SNSPDs) are promising for future quantum technologies. Nevertheless, their performance is limited by thermal-induced latching and detection band limits. In order to overcome these limitations, we propose to develop hybrid systems based on tungsten carbide (WC) nanowires on top of a graphene field effect transistor (GFET). Electrical and electro-optical measurements will be carried out in vacuum under cryogenic conditions (4K).

Introduction

SNSPDs have very high performance and sensitivity¹. Nevertheless, their operation is restricted to very low temperatures ($T < 4.2\text{K}$) increasing the cost and complexity². When a photon hits the nanowire, it breaks Cooper pairs, generating a hot-spot with a finite resistance and, hence, a voltage pulse can be detected. They exhibit very low Dark Count Rate (DCR), low jitter, high detection efficiency, fast time response and polarization sensitivity. However, they have limitations related to the latching or reset time which originates from thermal conductance. Their operating frequency band is also limited to the superconducting bandgap.

We propose a new approach based on the fabrication of hybrid systems based on WC and graphene in order to reduce latching and reset². It is known that detectors based on 2D materials exhibit remarkable optical performance. Our strategy consists of growing superconducting nanowires made of tungsten carbide on top of a GFET³ with superconducting source-drain electrodes. Due to the high thermal conductivity of graphene, a fast thermal relaxation of the hot-spot is expected and, therefore, a reduction of the latching effects.

Experimental

The GFET devices are fabricated by chemical vapor deposition, standard lithography and lift-off methods on SiO₂/Si substrates. The WC nanowires are produced via pulsed focused electron beam induced deposition (PFEBID) onto the graphene monolayer. They are characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy micro-Raman, and photo-voltage time-resolved spectroscopy at low temperature (LT) and high vacuum conditions.

Results and discussion

The WC nanowires have been fabricated (Figure 1) onto SiO₂/Si using 2ms pulsed at 2.5kV with a beam current of 220pA and a total of 200 loops. Aspect ratios higher than 2000:1 can be obtained by this method.

Conclusions

To our knowledge, this is the first time this fabrication scheme has been employed for the development of similar practical devices⁴. Based on the electrical characterization, further optimization of the nanofabrication process will be performed in order to fulfil the requirements of sensitivity of the fabricated detectors. This research might contribute to the development of quantum technologies, for example, for its use as a single-photon detector in quantum key distribution experiments.

Acknowledgments

This work is partially supported by the Spanish MICIN-AEI through Grants DETECTA ESP2017-86582-C4-3-R and EQC2018-005134-P. Also, by the Comunidad de Madrid through Grant P2018/NMT-4291 TEC2-SPACE-CM. A.G. and D.G. acknowledge the Office of Naval Research Global for financial support through Grant ONR-G #N62909-19-1-2053 (DEFROST). IMDEA Nanociencia acknowledges support from the "Severo Ochoa" Programme for Centres of Excellence in R&D (MINECO, Grant SEV-2016-0686). A.G. acknowledges ESP2017-83921-C2-1-R, ESP2017-92706-EXP and IJCI-2017-33991.

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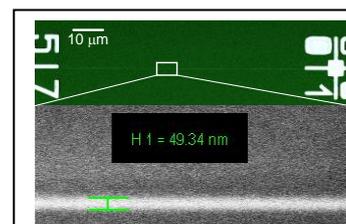


Figure 1. (Top) SEM image of a 100 μm long WC nanowire between to gold electrodes acquired ad 2.5kV with beam current of 220pA. (Bottom) Zoom-in demonstrating a wire width of <50nm. The total aspect ratio of the WC nanowire is higher than 2000:1.

Langmuir-Blodgett Biosensors based on Substituted Metallic Phthalocyanines and the Influence of the Enzyme-Mediator Interaction in the Electrochemical Detection of Galactose

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The good performance of Phthalocyanines (Pcs) in Langmuir-Blodgett (LB) films in the development of electrochemical sensors is well-known due to Pcs' electrocatalytic properties that are enhanced when in a nanostructured arrangement [1,2]. Moreover, Pcs' electrochemical properties can be modified by adding substituents to the aromatic ring [3]. In the present work, nanostructured voltametric biosensors for the detection of galactose were developed using the Langmuir-Blodgett (LB) technique. Tetracarboxy Iron Phthalocyanines (TCFePc) were used to improve the electron transfer catalyzed by the galactose oxidase (GaOx) between the solution and the ITO substrate. The influence of the GaOx-TCFePc-ITO arrangement and interaction between the GaOx and TCFePc were studied. The GaOx-TCFePc-ITO LB films were characterized by means of their Langmuir isotherms, Brewster Angle Microscopy (BAM), UVVis, FTIR and AFM. The electrochemical performance is being studied for different enzyme-mediator configurations, as Figure shows i.e. GaOx drop-casting on the TCFePc LB film, GaOx addition underneath the TCFePc floating monolayer before LB deposition, and covalent bonding between the GaOx amino groups and the carboxy groups of TCFePc. It is expected to find a low detection limit with different sensitivity and selectivity depending on the type of configuration, due to the interaction between the layer and the biological material.

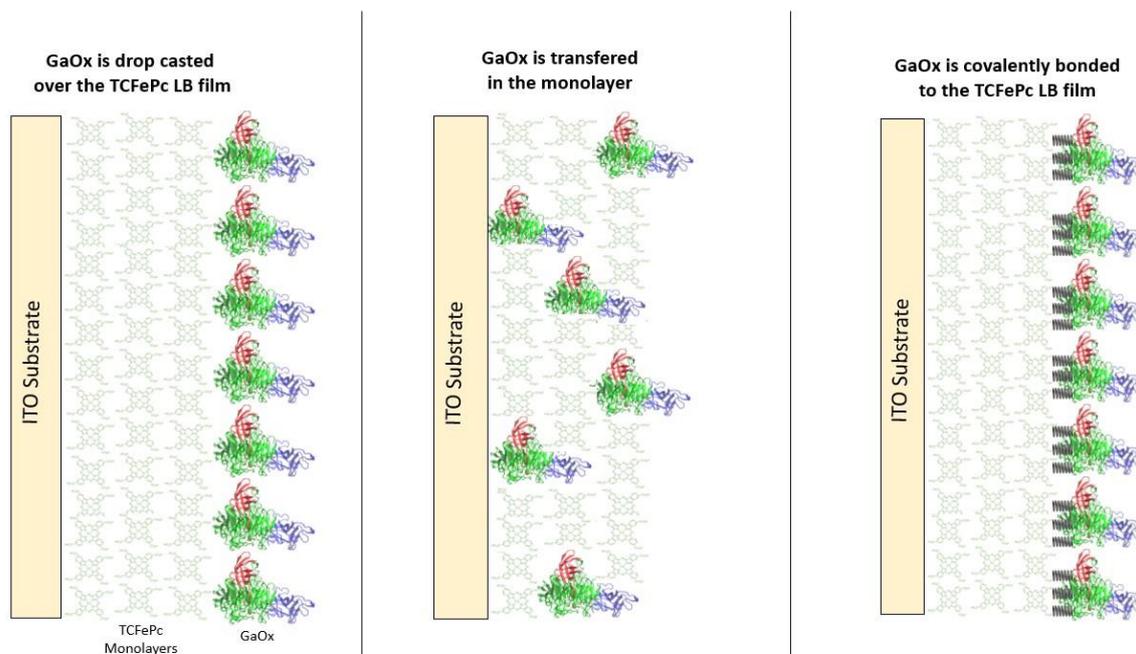


Figure: Scheme of the different configuration for the LB films.

Acknowledgments: MICINN-FEDER Plan Nacional (RTI2018-097990-B-100), Consejería de Educación Junta de Castilla y León- FEDER VA275P18 and «Infraestructuras Red de Castilla y León (INFRARED)» UVA01

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Hydrogen production by water splitting technique using $(g-C_3N_4)_x(CdS)_{1-x}$ as photocatalyst.

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The present study focuses on the study of photocatalysts oriented to the production of hydrogen using solar radiation as a source of energy. Catalysts based on cadmium sulphide (CdS) and carbon nitride with graphitic structure ($g-C_3N_4$) have been synthesized. In addition the $g-C_3N_4$ decorated with CdS have been fabricated with different ratios. The pure catalysts and their composites have been characterized by DRX, SEM and TEM. The hydrogen production was in a homemade setup designed for us. The photocatalytic setup consists of a reactor, a stainless steel ellipsoidal cylinder as reflector, two radiation lamps (Vis and UV) and a mass spectrometer for monitoring the hydrogen evolution. The decorated $g-C_3N_4$ catalysts exceed the hydrogen production rate obtained with the commercial photocatalyst P25, based on TiO_2 , which was used as a reference. The higher hydrogen production rate was achieved for the CdS/ $g-C_3N_4$ ratio of 5/3 (w/w), which was 10 times higher than the values obtained for pure CdS.

This work has been financed for MINECO through MAT2016-80933 project

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Silicon Phtalocyanine-Based Surface Functionalized Metal-Organic Frameworks as Active Materials in Optical Cavities

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Metal-Organic Frameworks (MOFs) are supramolecular structures generated by the mix of organic molecules and metal atoms. This kind of structures have been increasing its importance, showing to be useful in a huge variety of areas such catalysis^{1a}, gas purification and storage^{1b} or charge transfer. Lately, and especially in applications related to nanotechnology, it has become necessary to immobilize these structures onto a solid substrate, forming the so-called SURMOFs (surface-supported MOFs). SURMOFs can be obtained in different ways, including layer-by-layer (lbl), electrochemical and vapour phase deposition methods, in which the orientation and thickness of the MOF layer are precisely controlled.²

Silicon phthalocyanines (SiPc)³ are very interesting compounds for the generation of MOFs and SURMOFs. Due to its chemical versatility, a number of different substituents can be introduced in peripheral, non-peripheral and axial positions. And, importantly, this variety in functionalization does not compromise the necessary molecular symmetry for non-covalent interaction with metal atoms and generation of a three-dimensional structure.

Here we present the synthesis of a series of SiPc compounds, axially functionalised with different length carboxylic acid appends (Figure 1a), and the evaluation of its capability to generate, in combination with Zn atoms, SURMOF structures employing a lbl deposition method grown on SAM-modified Ag surface (Figure 1b). These nanoporous frameworks behave as active materials in optical cavities.⁴

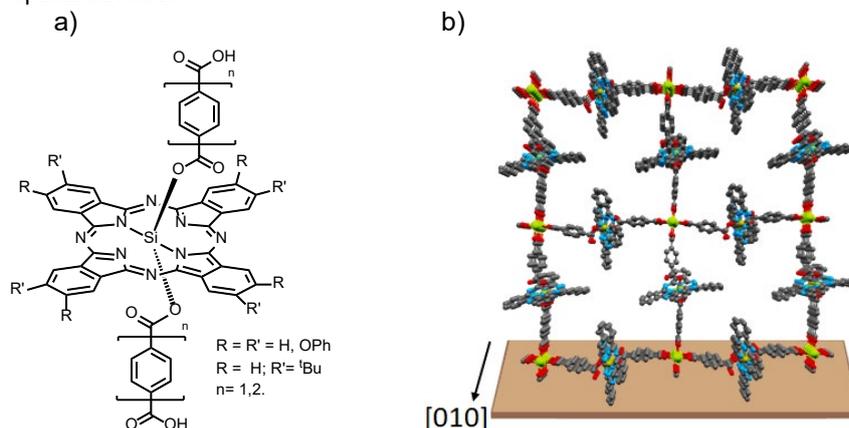


Figure 1. a) Molecular structure of the different SiPc synthesized. b) Zn-Si-Pc SURMOF grown on SAM-modified Ag.

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Solvent-free synthesis of CsPbBrI₂ for photovoltaics

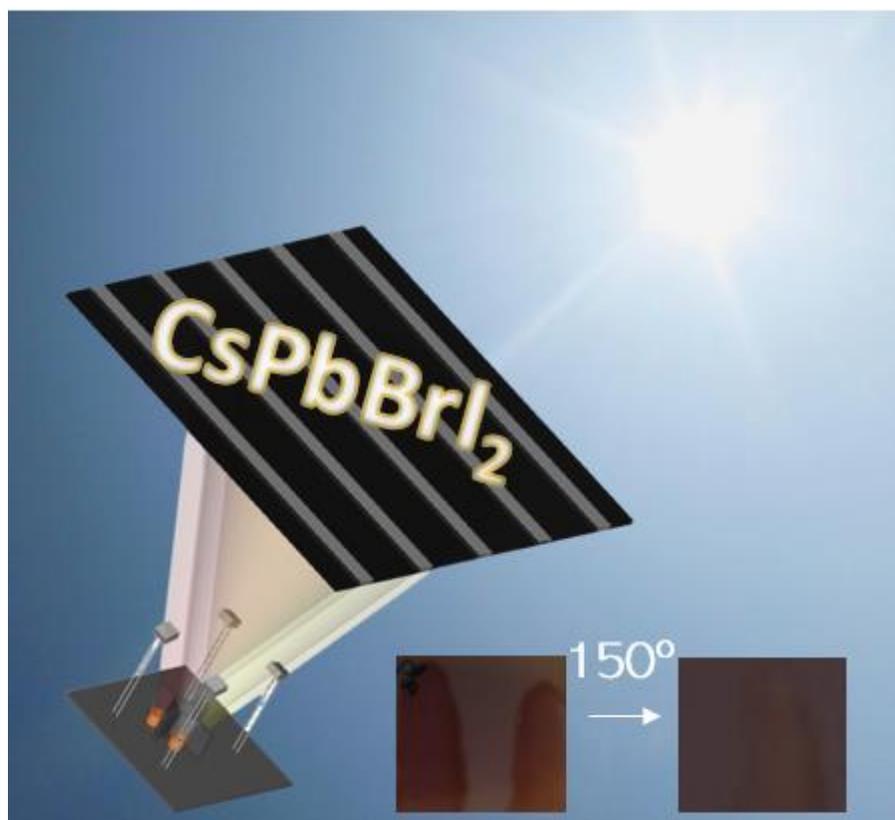
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Cesium-based perovskites have shown to be promising materials for solar cell applications, with power conversion efficiency exceeding 18% for the mixed halide compositions.¹ In general, the black perovskite phase is not stable at room temperature and hence very high temperature annealing are used to stabilize the material.² The substitution of iodide by bromide within the perovskite structure has proven to decrease the temperature needed to form and stabilize this phase.³ However, metal bromides are poorly soluble in the solvents commonly used to process perovskite films. In this work, different approaches to deposit CsPbBrI₂ films by sublimation methods are presented, with an emphasis on the material growth at room temperature as a function of deposition rate and type/number of precursors. We obtain smooth and pinhole-free films at room temperature, with high control over the thickness of the layers. Solar cells are prepared employing only sublimation methods (for both the perovskite and the selective contacts) and their photovoltaic performance is studied as a function of the synthetic approach.



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Selective Transport Metal Oxides

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Due to the demand and boom of new applications, as is the case for example of the synthesis of efficient solar cells that are committed to the use of optimal renewable energies, new nanomaterials with certain properties depending on the desired application have appeared. Within this broad group of nanomaterials are metal oxides, which have a wide range of applications depending on the transition metal used and also, as here we present, they can be easily synthesized through a straightforward procedure.

Metal oxide semiconductors such as TiO₂, SnO₂, CoO, In₂O₃, MoO, ZnO, etc., show very interesting properties with application in different areas of science depending on their properties such as electrical conductivity, optical transmittance, redox properties, photoreactivity, etc. For instance, metal oxide semiconductors are used in optoelectronic equipment, such as organic light emitting diodes (OLEDs), inorganic light emitting diodes (LEDs), organic photovoltaic (OPVs) and inorganic photovoltaic (PVs), among others. For this reason, optical, electrochemical and surface characterization is necessary to be performed, depending on the final application. For example, electron and hole transport layers (ETL and HTL) that are used on solar cell, requires a high electron and hole mobility, as well as a high transmission and stability^[1]. Thus, once the metal oxide has been synthesized, a complete characterization is essential.

This abstract, which shows a few light brushstrokes of the Final Master's Project that is currently being carried out, is based on the solution-processed in-situ synthesis of different metal oxide thin films synthesized from a simple and inexpensive process. This procedure, known as the sol-gel technique, is an easy and versatile manner for the preparation of nanocomposites as a nanoinks which can be used through different deposition-printing techniques making them so attractive at industrial level. In addition to this, it should be noted that the fact of working with a solution allows tunability by doping or imbibing other metals within, noble or not, in order to achieve certain properties of interest.

The synthetic pathway consists of the deposition of a precursor formulated in solution on the surface of a selected substrate^[2] through the spin-coating technique. The precursor solution contains the transition metal salt and the solvent in the correct amounts, since the concentration of the precursor is a parameter to be taken into account in the subsequent characterization. Once the precursor has been coated on a substrate, the sample is baked to a certain temperature and for a certain period of time. Different parameters such as precursors concentration, baking time and temperature and spin-coating conditions (spin rate and time) are used to optimize the final properties of our materials.

Figure 1, shows the transmittance of obtained for CoO films spincoated from a 0.7 M Co(AcO)₂ in methoxyethanol and baked for different times at 200°C.

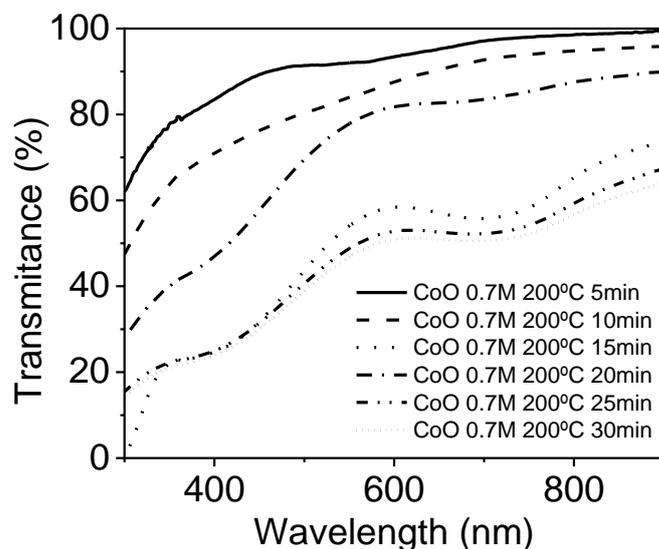


Figure 1. Transmittance as a function of wavelength for glass substrates where a CoO layer has been deposited through the Spin-coat technique, working with a concentration of 0.7M, 200°C, different template times: 5, 10, 15, 20, 25, 30 min.

As observed, in obtaining a metal oxide, in this case CoO, the parameters that specify the synthesis process are extremely important, since they give it the characteristics and subsequent applications.

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Semi-transparent metal thin-film electrode-based perovskite solar cells

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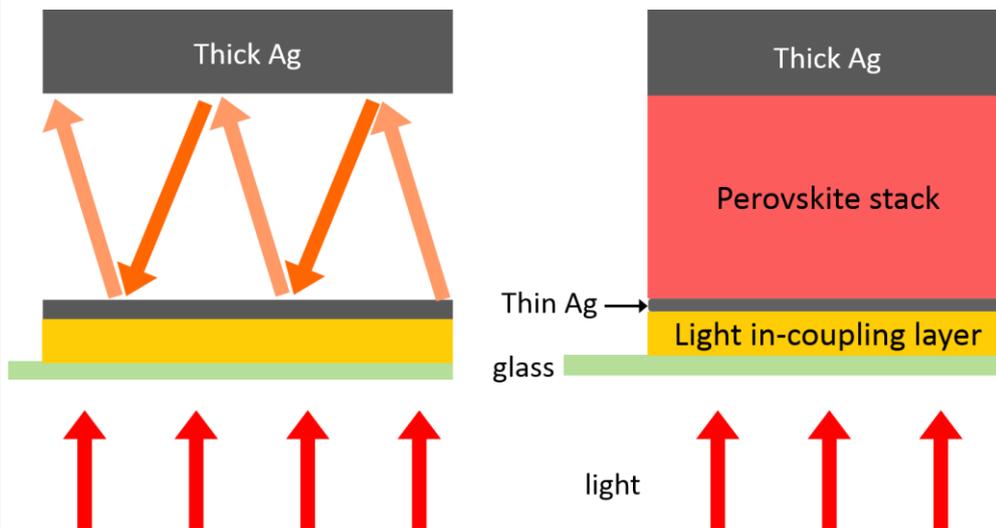
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Ultra-thin silver (Ag) films having low percolation threshold could be the potential alternative of the commonly used ITO electrodes for solar cell application. Their prime advantages over the ITO electrode include low-material or thinner film requirement (~10 nm) [1], formation of optical micro-cavity with the reflective metal rear-electrode for the resonant-trapping of light [2], and compatibility with low-temperature flexible substrates [3]. Lead halide perovskites are promising material for harnessing solar energy as single-junction perovskite solar cells are now known to demonstrate efficiency as high as 25.2% [3]. Integrating thermally evaporated Ag thin films with sublimable perovskite and charge transport layers offers an attractive and facile thermal evaporation based avenue of complete front-to rear electrode fabrication of efficient perovskite solar cells on bare glass substrates. In this work, we demonstrate the fabrication and characterization of metal thin film electrode derived unique inverted perovskite solar cell architectures and discuss the advantages and issues associated with using metal thin films as the perovskite solar cell's front electrode.

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Design and development of a potentiometric e-tongue with nanomaterials for the dairy industry

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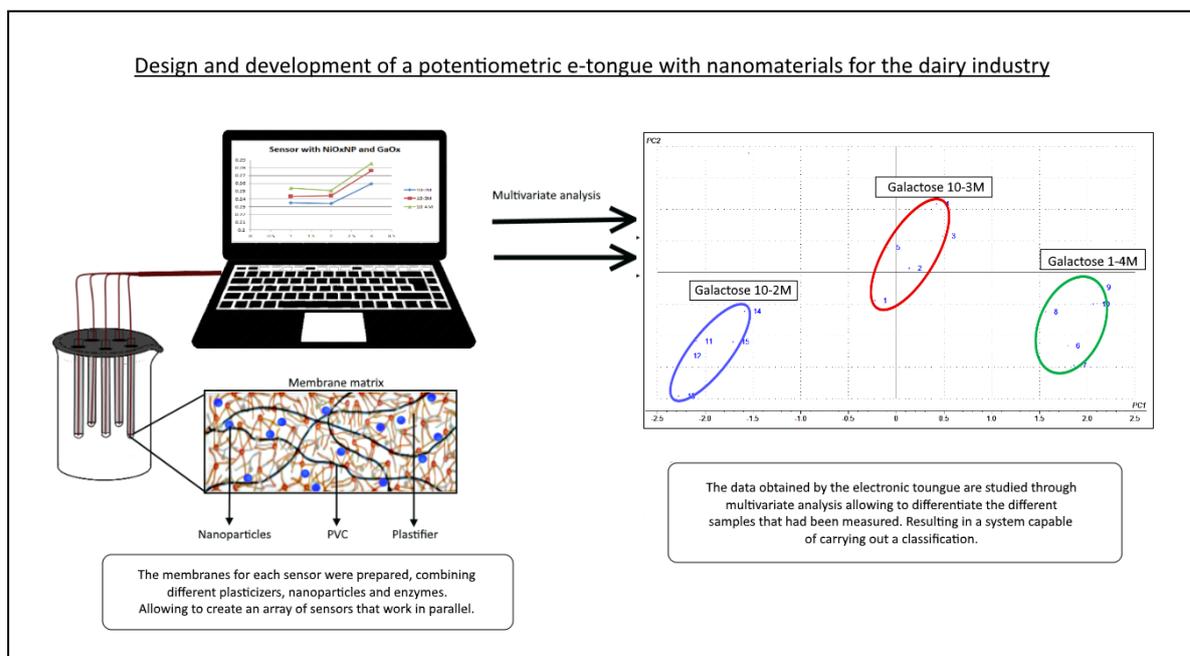
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The concept of electronic tongues has developed rapidly during recent years due to their large potential to discriminate and analyse foods and beverages as sensing technologies that greatly contribute to quality management. They are based on sensor arrays with low selectivity and high cross-selectivity and a capability of statistically analysing the outputs from multiple sensors [1].

The aim of this work was to construct an all-solid-state potentiometric e-tongue with an array of sensors based on polymeric membranes each working in parallel, in which the polymeric mixtures were applied on solid conducting silver-epoxy supports, to be applied in the dairy industry.

In order to obtain an array of sensors with cross-selectivity, the membranes were modified with gold nanoparticles [2]. In addition, enzymes as galactose oxidase, urease and lactate dehydrogenase were covalent bonded to the PVC surface to increase the selectivity of the sensor.

The results obtained with the potentiometric electronic tongue demonstrated that the system developed is able to detect components found in milks (such as acid lactic, galactose or urea) which could be used to discriminate and classify milks with different characteristics.



Acknowledgments: MICINN-FEDER Plan Nacional (RTI2018-097990-B-100), Consejería de Educación Junta de Castilla y León- FEDER VA275P18 and «Infraestructuras Red de Castilla y León (INFRARED)» UVA01

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One- vs two-step Spin Crossover modulation through host-guest chemistry in amino-functionalized 2D Hofmann-type coordination polymers

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In this work we report a novel family of Spin Crossover¹ (SCO) 2D Hofmann-type coordination polymers (2D-HCP) formulated as $\{\text{Fe}(\text{5-NH}_2\text{pmd})_2[\text{M}^{\text{II}}(\text{CN})_4]\cdot\text{H}_2\text{O}$ [5-NH₂pmd = 5-aminopyrimidine, M^{II} = Pt (**1^{Pt}·H₂O**) or Pd (**1^{Pd}·H₂O**)]. Both frameworks exhibit a two-step spin transition stemming by the presence of two crystallographically distinct Fe^{II} ions generated by the presence of host-guest interactions. Upon heating both compounds up to 400K, a single-crystal to single-crystal loss of guest water molecules is induced, driving to the corresponding **1^{Pt}** and **1^{Pd}** dehydrated counterparts. These desorbed compounds display complete single-stepped SCO curves explained by the existence of a unique type of Fe^{II} center in the bimetallic framework. Furthermore, the activated **1^{Pt}** and **1^{Pd}** compounds are able to re-adsorb either molecules of water, even in atmospheric conditions, recovering the original two-stepped SCO behavior or methanol/ethanol which partially block the HS → LS transition of the resulting **1^M·MeOH** and **1^M·EtOH** frameworks. Time dependent isotherms have also been performed to study the adsorption properties of the activated compounds exposed to different guests. The efficient modulation of the SCO properties through host-guest chemistry, primarily assisted by the tendency of the amino group to form hydrogen bonds, makes the reported 2D-HCP system a powerful platform for the development of future sensor devices.

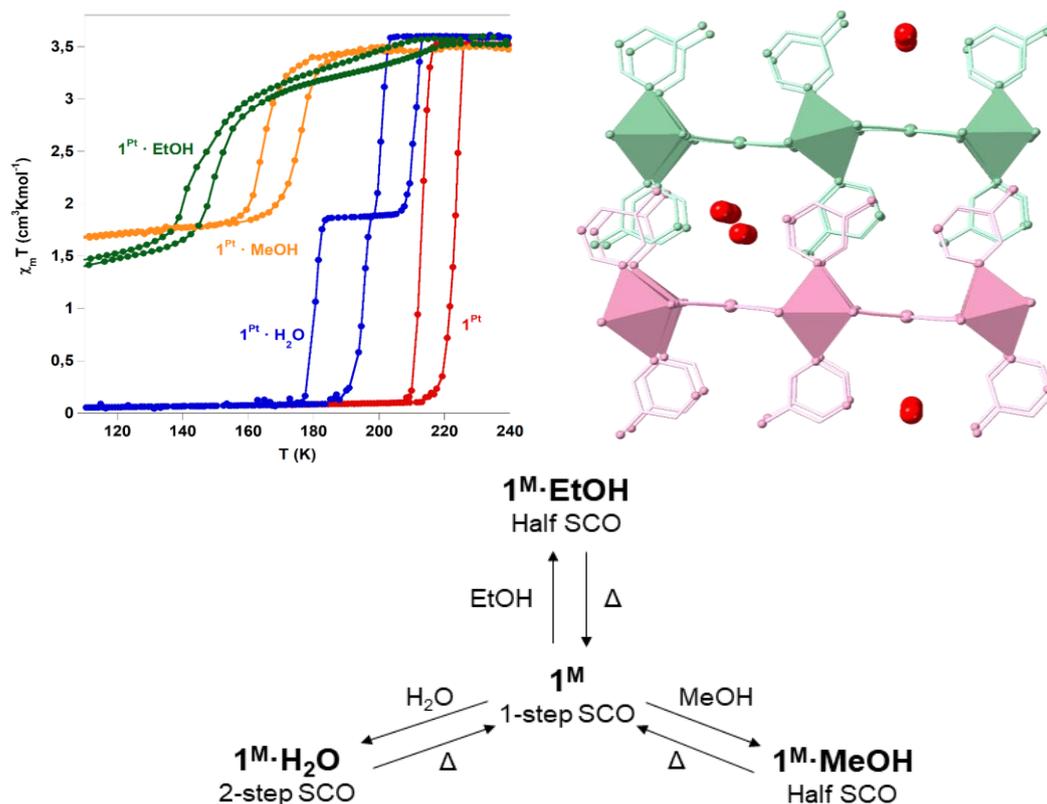


Figure 1. (Top Left) Magnetic properties of the **1^{Pt}·Guest** derivatives. (Top Right) Fragment of the structure. (Bottom) Scheme of the synthetic procedure for the presented compounds.

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Comparison between top-down and bottom-up synthetic approaches in production of antimonene for both cell internalization and cell viability.

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Nowadays, nanostructures based on antimonene, a novel two-dimensional (2D) material, have attracted great interest due to their appealing physical and chemical properties, such as high carrier mobility, layer-dependent tunable bandgaps, strong spin-orbit coupling, superior catalytic activity, and stability in ambient conditions.

Moreover, it has been demonstrated the excellent properties of the antimonene in photoabsorption and photothermal conversion mechanism [1]. For this reason, several studies have been published about the capabilities of antimonene biomedical applications, such as cancer treatment and photodynamic therapy.

Photodynamic therapy is a promising and non-invasive therapy for the treatment of oncological and non-oncological diseases. This treatment consists of systemic application of the photosensitizers which upon activation by light of specific wavelength, triggers a cascade of toxic photoreactions inducing the death of surrounding cells. Because of the minimal toxicity in the absence of light and being toxic only upon photoactivation, is an excellent recourse for the selective damage in the cancerous cells, for example. Despite the fact that antimonene has been shown to be a promising material for its application in photodynamic therapy, many questions remain to be resolved, such as its biocompatibility or its successful cell internalization as a function of the surface oxidation

To face this challenge, herein we have synthesized antimonene via different approaches in order to testing the cell viability and cell internalization. If we succeed, we will pave the way for the use of antimonene as a carrier for photodynamic therapy.

The preparation of the antimonene with different size, shape, morphology, and oxidation degrees has been carried out by top-down and bottom-up approaches, in order to check the different responses that it can generate in the cells. Concerning top-down approaches, we have prepared antimonene quantum dots by conventional liquid phase delamination strategy, using ethanol as a solvent [2], as well as antimonene nanosheets by ultrasonication-assisted liquid phase exfoliation [3].

Focusing now on the bottom-up approaches, we have prepared few-layer hexagonal antimonene nanosheets via colloidal chemistry [4].

Finally, testing the cell viability and cell internalization will take place in both cells' lines: healthy fibroblasts and HeLa cells.

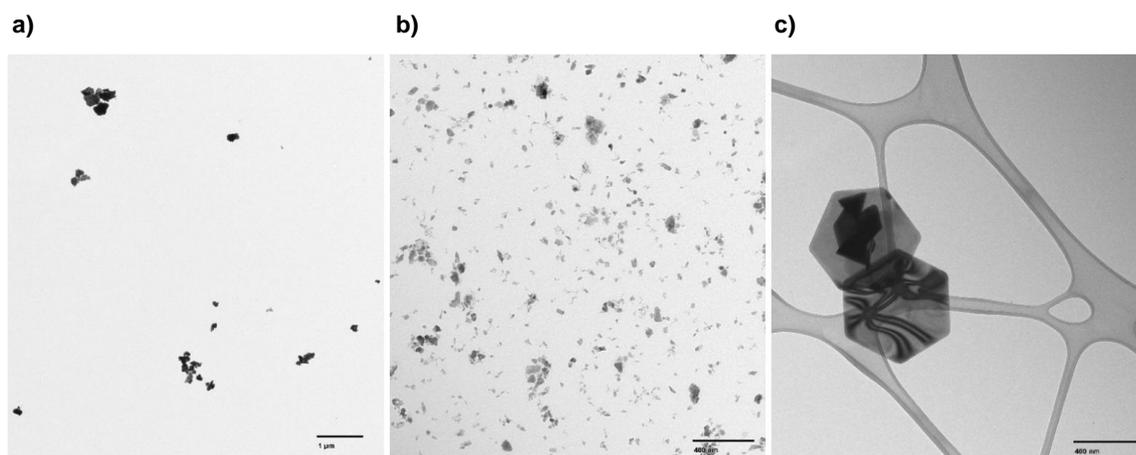


Figure 1. a) Antimonene nanosheets. b) Antimonene quantum dots. c) Hexagonal antimonene nanosheets.

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