25 Anys de
Ciència dels Materials

25 Years of
Materials Science

ICMUV
INSTITUT DE CIÈNCIA
DELS MATERIALS de la
Universitat de València

VNIVERSITAT DE VALÈNCIA

GENERALITAT VALENCIANA
Conselleria d'Innovació,
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i Societat Digital

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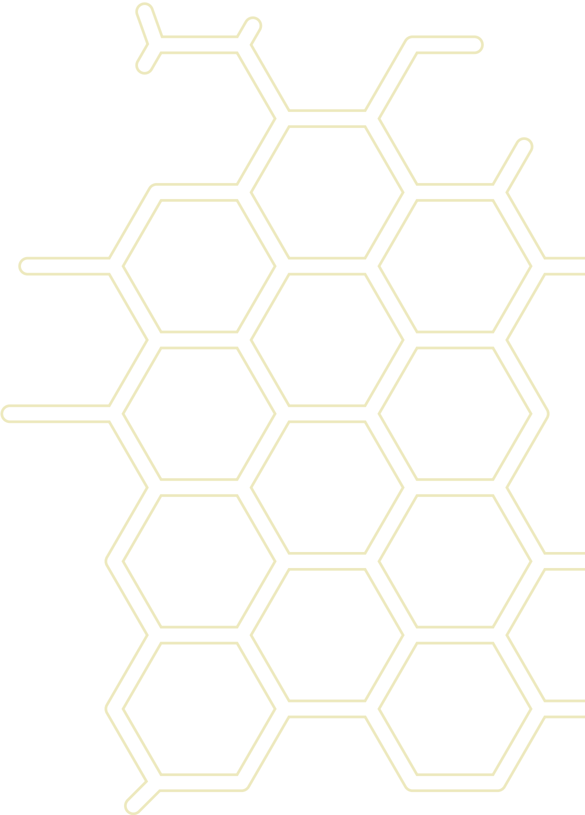
La presente publicación forma parte de la subvención, de la Universitat de València y de la Conselleria d'Innovació, Universitats, Ciència i Societat Digital de la Generalitat Valenciana, para la organización y difusión de congresos, jornadas y reuniones científicas, tecnológicas, humanísticas o artísticas de carácter internacional (AORG 2020), y en concreto de la correspondiente a la organización del Congreso: 25 Anys de Ciència dels Materials/ 25 Years of Materials Science (AORG/2020/A/021)

Esta publicación está disponible gratuitamente, en formato pdf, en el apartado de publicaciones de la página Web: 25 Aniversario ICMUV, con el fin de facilitar su acceso a la comunidad educativa.

El ICMUV expresa su más sincero agradecimiento a todas las personas e instituciones que han colaborado desinteresadamente con la cesión de textos e imágenes.



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PRÓLOGO

Mª Vicenta Mestre Escrivà

Rectora de la
Universitat de València

La Universitat de València es una universidad pública, abierta al mundo, comprometida con su territorio y vinculada a la sociedad valenciana desde su creación en 1499 por los Jurados de la ciudad de Valencia. Docencia, investigación, innovación y transferencia del conocimiento en todas las áreas del saber, unida a un gran sentido de la responsabilidad social y un extraordinario dinamismo cultural y de divulgación son pilares fundamentales de la institución. Son, asimismo, base para el fortalecimiento del prestigio científico nacional e internacional fruto, entre otras razones, de la excelente actividad de sus grupos de investigación, estrechamente ligada a la de los Institutos Universitarios. Entre ellos, la Universitat de València tiene el honor de contar con el Instituto de Ciencia de los Materiales (ICMUV), institución que, desde su creación hace 25 años, ha favorecido de manera indudable el avance del conocimiento y la divulgación científica, aportando a la sociedad las mejores soluciones ante las necesidades y problemas que la esencia misma de la realidad plantea.

Nuestra Institución ha visto, con inmensa satisfacción, cómo los miembros del Instituto del ICMUV han logrado materializar todas estas aspiraciones en el desarrollo de numerosos proyectos, captando financiación procedente tanto de la Unión Europea como de entidades nacionales y autonómicas. Paralelamente, han desarrollado numerosos proyectos junto a las industrias de nuestro entorno, propiciando la creación, en el seno del Instituto, de cuatro empresas Spin-off.

En un contexto en el que todas y todos debemos hacer un gran esfuerzo por retener el enorme talento con el que cuenta nuestra sociedad, hay que destacar especialmente la iniciativa del Instituto por dar protagonismo a sus jóvenes investigadores a través de la celebración anual de las Jornadas Jóvenes ICMUV. Jornadas con un marcado carácter internacional, orientación hacia la excelencia y vocación de impacto científico aprovechando, y a su vez ayudando a consolidar, la proyección internacional de la Universitat de València en Europa y el mundo.

Quiero también aprovechar estas líneas para hacer una mención especial a las mujeres científicas que trabajan en un ámbito tradicionalmente masculino como este, y en especial en este momento concreto a la directora del instituto, la profesora Ana Cros. Sin duda, investigadoras de este nivel abren la puerta a otras mujeres en la investigación y a la creación de referentes en mayúsculas en un camino tan interesante y necesario como es la investigación en ciencia de los materiales, todo en un contexto complejo, a la par que estimulante para el pensamiento científico, como el que vivimos.

Estas ideas se han plasmado en el libro que ahora tengo el honor de prologar, como rectora de esta universidad, y donde se incluye una perspectiva de las líneas de investigación del ICMUV, así como una visión general del estado actual en el ámbito de la Ciencia de los Materiales, a través de los resúmenes de las distintas ponencias científicas que tuvieron lugar en la celebración de este evento. Poco más de cincuenta páginas de consolidación de conocimiento, experiencia y riguroso trabajo científico que no puede más que enorgullecer a la institución y justificar el reconocimiento y gratitud de su rectora.

PREFACIO

Ana Cros

Directora del ICMUV

Estimados compañeros, patrocinadores, estudiantes y colaboradores del Instituto de Ciencia de los Materiales de la Universitat de Valéncia.

Sí, ya son 25 los años que han transcurrido desde que, allá por 1995, un conjunto de personas, lideradas por nuestro compañero Daniel Beltrán, decidieran aunar sus esfuerzos de investigación y poner en marcha el ICMUV. Profesores, profesoras y estudiantes con entusiasmo y ganas de utilizar la ciencia de materiales como puente de unión entre campos como la física, la química o la ingeniería. No fue hasta 1999 que el ICMUV pudo contar con una sede central donde albergar algunos de nuestros despachos y laboratorios: el Edificio de Institutos de Paterna. Este tiempo no ha transcurrido sin obstáculos, algunos de carácter acuático (2001), otros presupuestarios (2008); imprevistos que ahora, en el 2020, han quedado superados por el desafío de la Era COVID. Sin embargo, el tropiezo más doloroso ha sido la pérdida de algunos de nuestros compañeros. Tenemos su recuerdo bien presente.

25 años de andadura: superada la adolescencia, nuestro ICMUV ha expandido sus capacidades con la incorporación de nuevos grupos de investigación,

nuevas técnicas, proyectos y personas. El ICMUV se adentra en un periodo de madurez que permitirá consolidar sus colaboraciones interdisciplinares y afianzar una proyección internacional ya muy avanzada.

Me queda tan solo desearos salud y energía para abordar los retos que tenemos ante nosotros.

RESEARCH LINES

ARCHAEOMETRY UNIT

Clodoaldo Roldán García, Sonia Murcia Mascarós

The application physico-chemical techniques (initially developed in the field of materials science) to the study of Cultural Heritage materials provides reliable qualitative and often quantitative information on the considered objects. By this way, it is possible to understand, for instance, the technical and intellectual know-how of the artists or craftsmen of the period under study, and to obtain the preliminary often essential information for art historians, archaeologists, restorers and curators (elemental and/or molecular composition, degradation processes, corrosion patinas, …) and to assess the authenticity of artefacts in many cases. On the other side, availability of a portable apparatus represents a strong constraint for many analyses to be performed in situ, since artworks of large dimensions or particularly fragile cannot be easily and/or safely transferred to specific laboratories. The x ray fluorescence spectrometry and Raman spectrometry are then a suitable technology for this kind of analysis. The combination of these technologies with other analytical tools, all of them available at the ICMU, such as optical microscopy, scanning electron microscopy, x-ray diffraction, infrared spectroscopy and omic techniques, among others, allowed us to perform suitable analyses of pigments, lithic materials, ceramics, metal alloys, organic compounds, …

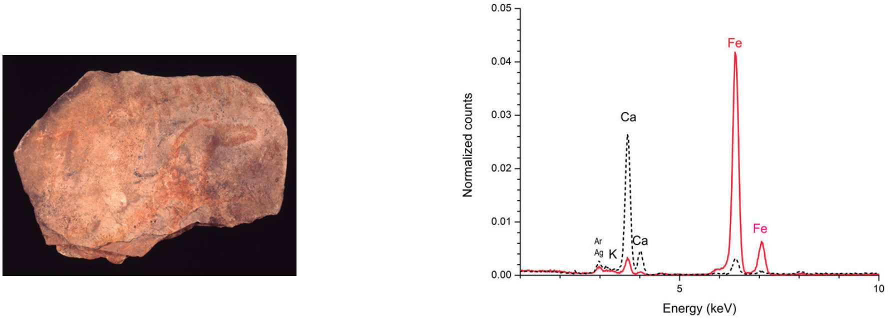
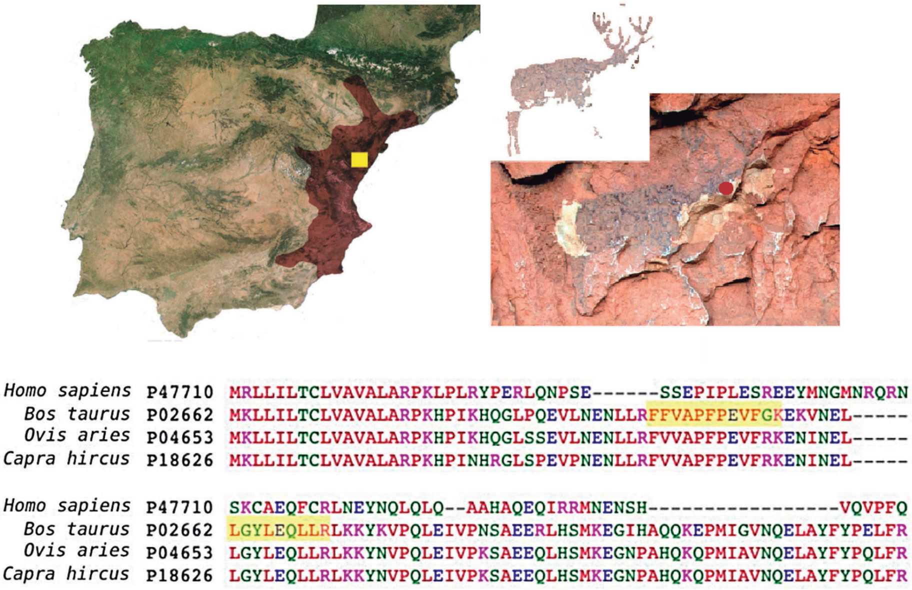


Figure 1. Example of analyzed plaquette from the Parpalló collection. Comparison between EDXRF spectra of iron red based pigments and that of the rock support.

In the last years, the Archaeometry Unit of the ICMUV has participated in projects related to the identification of pigments in portable Palaeolithic rock art and parietal Neolithic rock art of the Levantine region of Spain.

The Parpalló Cave covers a chronology between 23,500 and 14,000 years ago and its archaeological material consists of engravings and paintings made in more than 5,000 limestone plaquetttes that show the cultural expression of the hunting and gathering populations of the Upper Paleolithic of the Spanish Mediterranean region. Plaquettes from the cave (limestone with a flat surface and different thicknesses) showing on their surface zoomorphic, ramiform, and geometric representations executed with black, red and yellow pigments, have been analyzed by non-destructive techniques: energy dispersive x-ray spectrometry and spectrophotometry in the visible region. Red and yellow iron oxides (hematite and goethite), manganese blacks and carbon blacks have been identified as pigments [1, 2]. These results confirm that techniques and colorants identified are similar to the parietal figures of the same chronology. This coincidence is very interesting, since it constitutes an argument in favor of the similarity of the procedures used during the Paleolithic in movable art and in parietal art. On the other hand, the registration of the chromatic coordinates of the pigments is intended to serve as a starting point to document whether the painted surfaces of the plaquettes lose intensity or luminosity and to analyze their temporal evolution.

The Iberian Mediterranean arch houses a unique graphic manifestation in European prehistory: Levantine parietal rock art, declared a World Heritage Site by UNESCO in 1998. At present, the number of rock shelters decorated with these graffiti exceeds a thousand, being the core of Valltorta-Gassulla (Alt Maestrat, Castellón) one of the most outstanding territories due to the number of documented sites and the richness and interest of its panels. Levantine art is a pictorial tradition that is located in shallow shelters of the interior sierras. Its singularity, in clear rupture with all previous graphic manifestation, comes from its strong naturalistic and narrative component.



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Homo sapiens  P47710  MRLLILTCLVAVALARPKLPLRYPERLQNPSE------SSEPIPLESREEYMNGMNRQRN
  Bos taurus  P02662  MKLLILTCLVAVALARPKHPIKHQGLPQEVLNENLLRFFVAPFPEVFGKEKVNEL-----
  Ovis aries  P04653  MKLLILTCLVAVALARPKHPIKHQGLSSEVLNENLLRFVVAPFPEVFRKENINEL-----
Capra hircus  P18626  MKLLILTCLVAVALARPKHPINHRGLSPEVPNENLLRFVVAPFPEVFRKENINEL-----

Homo sapiens  P47710  SKCAEQFCRLNEYNQLQLQ--AAHAQEQIRRMNENSH-----------------VQVPFQ
  Bos taurus  P02662  LGYLEQLLRLKKYKVPQLEIVPNSAEERLHSMKEGIHAQQKEPMIGVNQELAYFYPELFR
  Ovis aries  P04653  LGYLEQLLRLKKYNVPQLEIVPKSAEEQLHSMKEGNPAHQKQPMIAVNQELAYFYPQLFR
Capra hircus  P18626  LGYLEQLLRLKKYNVPQLEIVPKSAEEQLHSMKEGNPAHQKQPMIAVNQELAYFYPQLFR
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Figure 2. Left: Geographic location of the La Saltadora shelter. Center: Sampled figure. Right: Multiple alignments of Alpha-S1-casein proteins of different origins Figures adapted from Scientific Reports, V 8, Article number: 10011 (2018).

These paintings represent economic and social activities – hunting, honey gathering or social conflicts – in which the male figure is praised in his role as hunter and warrior. The information potential of these paintings is enormous, and their study and documentation has the objective of knowing and characterizing the author societies. The composition of the pigments, that is to say, of the raw materials used during the elaboration of these paintings, is mainly composed of minerals based on iron oxides mixed with organic substances, which acted as binders, favoring their adhesion and resistance [3, 4]. Knowing these binders allowed us to understand the elaboration processes, although, identifying and characterizing these substances is complex due, among others, to the strong erosive process to which the Levantine shelters are subjected. Moreover, to identify the organic binding agents and the bacterial communities of the sites we have resorted to omic technologies, that is, those that study the totality of genes, organisms or proteins. It has been done through metagenomic techniques (science that studies the DNA of microorganisms, directly extracted from environmental samples) and proteomics (the massive biochemical study of proteins). We performed the first metagenomic analysis, that is, microbial DNA, directly obtained from micro samples from three painted motifs (an archer, a goat and a deer) and from a set of ‘control’ samples corresponding to the wall in zones without pictorial motives. Metagenomics has provided us with the first description of the bacterial communities that colonise the patina of rock art and parietal support, and that could have a protective effect on the paintings. On the other hand, the proteomic analysis of pigment samples from three figures has allowed to detect casein peptides of bovine origin in the samples analyzed. This finding allows us to hypothesize the use of animal milk as an agglutinating agent, thus opening the hypothesis that the societies that made these paintings practiced animal husbandry, thus situating themselves in a chrono-cultural framework typical of the peninsular Neolithic (VI-III). millennia BC). The research – in which the TRACES UMR 5608 laboratory of the Center National de la Recherche Scientifique de France (CNRS) and the company Darwin Bioprospecting Excellence, SL also participated –, has been developed with pigments from the Coves de la Saltadora shelter (Coves de Vinromà, Castellón), one of the most decorated sets of the Valltorta-Gassulla archaeo-cultural park.

This research was supported by the MICINN HAR2011-24878, HAR2014-52671 and HAR2017-85153; Generalitat Valenciana PROMETEOII/2013/016, PROMETEO/2017/060; CNRS-Mission Interdisciplinarité (2017-2019), MACOPREH.

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https://doi.org/10.1038/s41598-018-28121-6

FOOD & HEALTH LAB

Aránzazu González, M. Cruz Martínez, Jose M. Soriano, Carla Soler

Food & Health Lab of University of Valencia is a new research concept focused on users and supported in the open innovation and real scenarios. This initiative includes a series of actions to promote health, healthy and sustainable food strategies, nutritional intervention and improvement of the quality of life within the branches of the University, at a local, national and international level. It is aimed, on the one hand, to carry out health interventions in an interdisciplinary environment (with dietitians, nutritionists, food technologists, psychologists, geneticists, experts in preventive medicine, physiotherapist and experts in physical and sport activities), to increase the gastronomic and culinary strategies to adapt menus to individuals and/or patients and developing teams, methods and new tools in health environments, nutrition, gastronomy, physical activity and quality of life with applicability to society.

Food & Health Lab-University of Valencia is a space with the suitable conditions of active participation to know the social reality of health and food. Food&Health Living-Lab (Food&HealthLabLL) is the Living-Lab of the University of Valencia specialized in health, nutrition, physical activity and gastronomy that is part of the European Network of Living Labs (ENOLL).

It arises as an initiative of the Policies for Excellence Office (OPEX) of the University of Valencia and is funded by the institutional innovation programme of the OPEX and by the programme to promote innovative ecosystems of the Ministry of Education, Culture and Sports through the VLC/CAMPUS, Campus of International Excellence programme. Food&HealthLL is an innovation environment focused on service users and facilities of the University of Valencia. It aims at involving all actors (the university community and its productive and territorial environment), promoting innovative development and solutions for health, nutrition, food and physical activity problems from a diverse scientific focus. All in order to discover emerging scenarios and to support and explore new ideas, gathering market and technology and fostering the emergence of platforms for public-private action.

The specific units of the Food&HealthLL are encompassed in six categories (nutrition, gastronomy, physical therapy, psychology, physical activity and clinical-biochemical-genetic analysis lab activities). They are totally cross-disciplinary and interlinked within this new LivingLab.

In the last years, we are working to utilize molecular gastronomy to improve food textures for dysphagia diets, using techniques such as spherification, gelification, and emulsification [1]. On the other hand, this unit works in the analysis of food components, microorganisms [2] and pollutants, as well as on the development of new cooking tools. Our group is working from several extraction and clean-up methods from food and biological fluids [3], with genomic and proteomic analysis and determination of several compounds with chromatographic techniques. These studies are carried out with the financial support of the European, National and Local projects.

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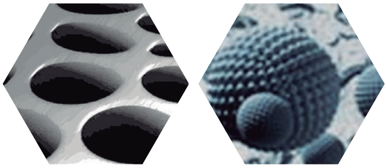
NANOSTRUCTURED MATERIALS GROUP (NMG)

Aurelio Beltrán, Francisco Pérez-Pla, Carmen Guillem, Jamal El Haskouri and Pedro Amorós



Although there is no single internationally established definition of nanomaterials (NMs), the NMs term usually refers to solids with a microstructure whose characteristic length scale is of the order of a few (typically 1-100) nanometers. Recently, the British Standards Institution proposed to extend the size scale to particles, aggregates or motives organized in a wider range (from 1 to 1000 nm). Then, both small objects (such as nanoparticles, small clusters, nanocomposites…) and also larger nanostructured materials (with an internal or surface organization at the nano-scale, as the nanoporous solids) can be included in the NMs category.

Nanoparticles (NPs) and nanostructured materials (NSMs) represent an active area of research and a rapidly expanding techno-economic sector in many application domains. Environmental pollution, energy consumption, medicine and biotechnology have induced more and more public concerns. Problems imposed by these issues will circulate in the 21st century. In this context, NPs and NSMs, as a transversal field, can provide a response and solution to some of the challenges that arise in the mentioned areas.

At the NMG we have focussed our research during the last decades in the area of porous solids, and more specifically on ordered mesoporous materials (OMM). OMM were unknown until 1992, when researchers of the Mobil Oil Co combined sol–gel chemistry with surfactant liquid crystal micelles to get the so-called M41S materials. After that, there was a worldwide explosion of research efforts towards OMM, as researchers now finally had the ability to synthesize materials with well-defined and organized pores at the mesoscale (adequate for emerging applications).

Our work on OMM has included both basic and applied aspects. Currently, in the ICMUV laboratories, we have the facilities, equipment and expertise to address a wide variety of challenges to which the OMM can respond. Our seminal work in this field dates back to the late 20th century, when we described the first ordered mesoporous oxides of aluminium and titanium synthesized with micelles of cationic surfactants as sacrificial templates [1]. This success was due to the development of a new synthesis strategy that we called the "Atrane Route", which is based on the use of complexes with ligands derived from triethanolamine as hydrolytic precursors [2]. The use of these precursors enables to balance the rates of the hydrolysis and condensation processes of the inorganic species as well as the self-assembling with the micelles. Since then, this methodology has allowed us to synthesize a great variety of nanostructured porous materials with very different compositions (inorganic, organic or hybrids) and pore architectures, including hierarchical porous materials as the UVM-7 [3] which combines meso and macroporisity (Fig.1).

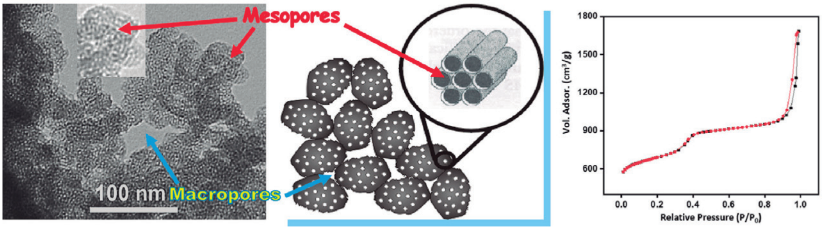


Figure 1.- TEM image, schema and N2 isotherm showing the combination of meso and macroporous in the UVM-7 silica (University of Valencia Materials, number 7).

Our working philosophy has been the synthetic design on the basis of well-founded chemical principles in order to solve target problems in various applied areas: catalysis, remediation, sensors and medicine. This goal has been approached thanks to the colla-boration with different national and international research groups.

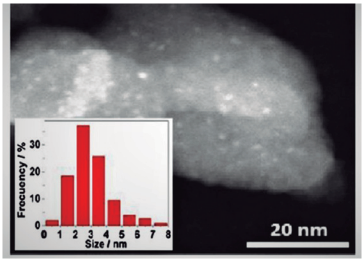


Figure 2.- Pd NPs on UVM-7 heterogeneous catalyst in the Suzuki-Miyaura reaction

In the catalysis field, we have developed different families of modified porous silica catalysts. The nature of the functional groups includes isolated heteroelements, small clusters, organic groups and metallic NPs (Au, Pd ...). These nanomaterials have shown excellent catalytic activity in processes such as epoxidation of bulky olefins, oxidative dehydrogenation of isobutane, carbon-carbon coupling reactions (Fig.2) [4] and environmentally friendly routes for the synthesis of fine chemicals. In other cases, the interest of the synthesized catalysts lies in their environmental benefits: degradation of VOCS and CO oxidation. In the latter case, the nanostructure of the catalysts shows exceptional thermal stability (Fig. 3), which makes these NMs widely applicable when severe working conditions are required, such as steam reforming or car exhaust control [5].

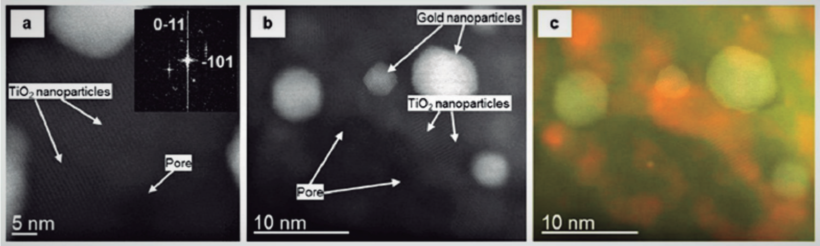


Figure 3.- Cs-corrected STEM-HAADF images of Au/TiO2/UVM-7 at 800ºC. (a) High-magnification image where the TiO2 nanoparticles are identified together with those of Au. The FFT of the TiO2 phase is shown as an inset. (b) Cs-corrected STEM-HAADF image where an EELS spectrum-image is recorded. (c) Ti-L3,2 (red) and O-K (yellow) maps superimposed on the HRSTEM-HAADF image.

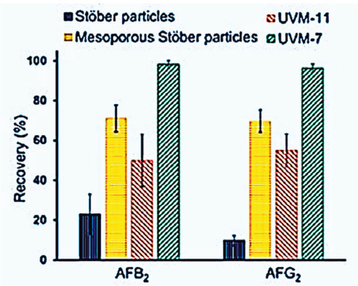


Figure 4.- Comparison of the recoveries for aflatoxins B2 and G2 by using silica materials with different architectures.

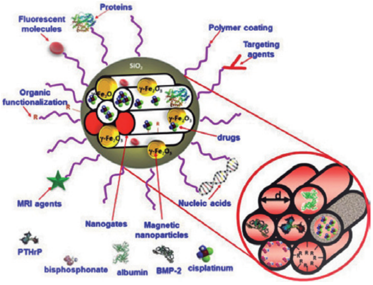


Figure 5.- Teragnostic materials based on OMMs.

In the field of remediation and environmental science, we have designed efficient alternative NMs for the capture and quantification of different polluting species, which include both traditional pollutants such as boron, polycyclic aromatic hydrocarbons and aflatoxins (Fig. 4), and also emerging polluting species such as polychlorinated biphenyls and flame retardants [6]. Analytical methods, even automated ones, in many cases involve sample preparation and eventually sepa-ration steps, with the consequent consumption of time and resources. To overcome these disadvantages, different functionalized NM-based sensor systems (responding to diverse stimuli) have recently been developed. We participate in the design of optical sensors benefiting from different strategies such as binding-site signalling subunit protocols, displacement reactions, chemodosimeters and gated OMM for the detection of a large variety of analytes [7]. Gated OMMs are a versatile tool to control mass transport. The most studied applications of these systems are related to controlled release protocols, especially focused on medicine. We also participate in the design of new materials for biomedical applications that combine the ability to deliver drugs for therapy [8] with diagnostic capabilities (teragnostic materials, Fig.5) thanks to the incorporation into the nanostructure of different species such as MRI contrast agents or UCNPs. These studies have been carried out with the financial support of the Spanish MICINN and FEDER funds.

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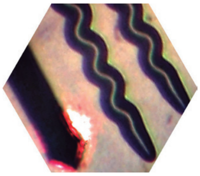
OPTOELECTRONIC PROPERTIES OF ADVANCED MATERIALS AND SURFACES (POEMAS)

Ana Cros, Núria Garro



The interdependence between optical and electronic properties of solids has led a great deal of the research in materials science in the last 50 years. New properties have been achieved when reducing the size and the dimensionality of the materials in structures such as quantum wells and dots, nanoparticles and nanowires or, since the isolation of Graphene in 2004, also 2D materials. It has been widely demonstrated that as size decreases, surfaces and interfaces begin to dominate the properties of nanostructured materials. Assessing electro-optical processes in these complex nanostructured materials is essential for improving both the efficiency and stability of emerging technologies. The performance of materials is usually quantified by macroscopic measurements, averaging out local heterogeneities that inherently exist in functional complex materials and hindering the observation of fundamental optoelectronic processes. Therefore, a thorough analysis requires techniques probing structure and dynamics of materials at the nanometer scale. At the POEMAS group, we combine several non-destructive techniques with spectral and dynamic resolution and multi-scale sensitivity to study semiconductor nanostructures and hybrid functional materials for energy harvesting and lightning applications.

In the last years, we have demonstrated the capabilities of atomic force microscopies (AFMs) to probe large ensembles of nanostructures while still providing enough spatial resolution to discriminate single nano-objects (see Figure 1). Our set-up offers three complementary AFMs techniques: Kelvin probe force microscopy (KPFM), which measures the surface potential; light-assisted KPFM to study optically driven process; and piezo-force microscopy (PFM) which can be applied to polar and piezoelectric materials. Figure 1 shows the topography of an ensemble of self-assembled GaN nanowires as recorded over a 3x3 μm2 area. The superimposed colour indicates the surface potential of each individual nanowire as measured by KPFM, which is indicative of its crystalline polarity. In spite of the irregular topography, KPFM shows very homogeneous and reproducible surface potential values associated to N-face polarity. Strong reduction of surface potential reveals the presence of a minority of Ga-polar nanowires (highlighted in the left picture in black) [1].

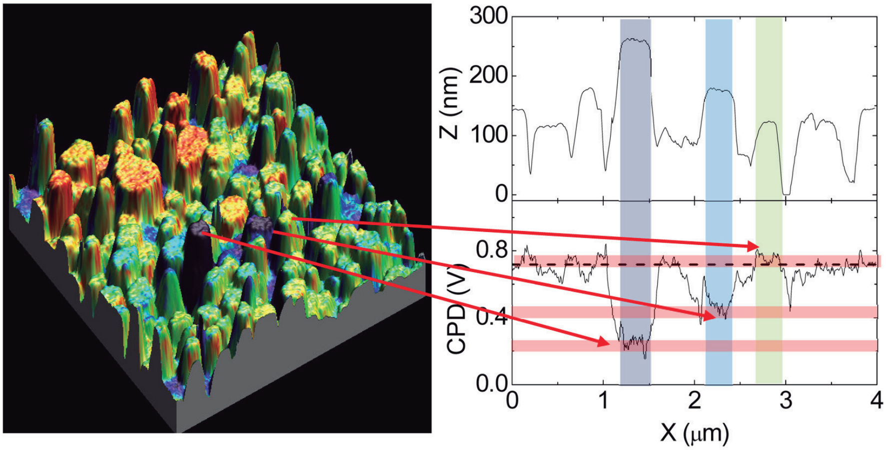


Figure 1 The polarity of self-organized GaN nanowires can be determined directly from the ensemble by topography and KPFM imaging. [1]

Our expertise also includes optical spectroscopy: Raman scattering and photoluminescence. Micro-Raman spectroscopy can determine the crystal quality, phase, strain state and composition with sufficient excitation density as to detect subtle changes in very small volumes of the material. Thus, different maps along the surface of heterogeneous materials allow achieving sub-micrometer resolution. These maps can be combined with AFM techniques to revel the surface electrical properties and their correlation with chemical composition. Figure 2 depicts an example of the potential of these techniques when applied to a GaN film grown on mica [2]. Under the compressive force exerted by the GaN film, the mica layers slide, giving rise to worm-like delaminations in the form of telephone cord buckles. The characteristics of the delaminations can be investigated by Raman scattering, determining their composition, strain and crystallographic phase. These results can be correlated to the three- dimensional topography of the buckles, with micrometer sizes, and their submicrometer granular characteristics, as obtained by AFM.

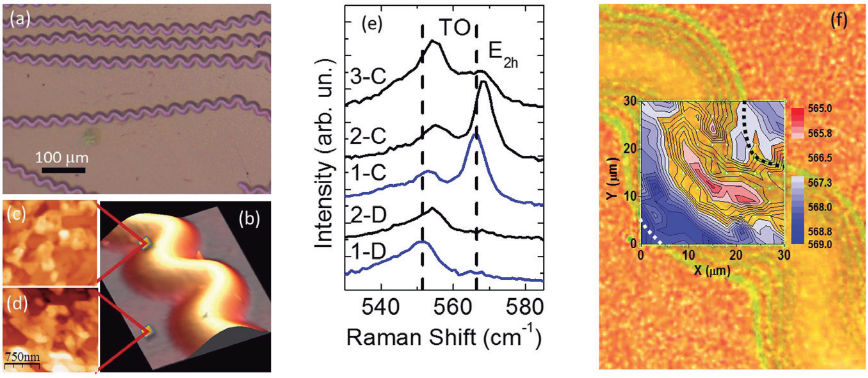


Figure 2 Morphology and strain of a GaN layer grown on mica. (a) optical microscopy and (b), (c), (d) AFM views of the topography of phone cord buckles; (e) and (f) Raman spectra and map along a single buckle showing different strains in the material. © IOP Publishing. Reproduced with permission. All rights reserved. [2]

These studies are carried out with the financial support of the projects PROMETEO2018/123 EFIMAT from Generalitat Valenciana and PID2019-104272RB-C53, co-financed by the Spanish MICINN and FEDER funds.

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POLYMER MATERIALS AT ICMUV

Clara M. Gómez and Rafael Muñoz-Espí

Polymer materials have received considerable attention in mass media in recent time, mainly from a negative perspective. But the reality is that polymer materials are not just “plastics”; and even the nowadays so “unpopular” plastics are not as evil as proclaimed sometimes. As a result of the extraordinary range of properties of polymers, they play an essential and in many cases irreplaceable role in everyday life. Since we get up in the morning until we go to bed at night, every minute of our life is surrounded by polymers. We can also not forget that biopolymers (including proteins, polysaccharides, and even DNA) are basic constituents of life. Keeping a responsible and sustainable use of polymers in mind, the mission of our group is to develop more environmentally friendly materials and to study their properties, adapting the functionalities to the specific requirements of companies and society in general.

The Polymer Materials Group at ICMUV focuses on the design, synthesis, and characterization of different types of polymer materials, including epoxy resins, polyurethanes, and conducting polymers. We also develop hybrid materials and nanocomposites, highlighting the importance of the interface in compatibilizing phases of different nature. Currently, we participate in research projects funded by different agencies, including the Spanish Government, the Max Planck Society (Germany), and private companies.

In addition to the research activities, our group is also engaged in the education and on-site training of students and young researchers. Tens of motivated Bachelor’s, Master’s, and PhD students have passed in the last few years through our labs, before jumping in their respective professional careers.

Current research topics

- Thermoplastic polyurethanes: design of new materials and characterization [1]
- Thermoelectric polymer materials: synthesis and characterization [2]
- Development of thermoelectric textiles by electrochemical deposition and layer-by-layermethods (schematic example of the methodology in Figure 1) [3]
- Polymer colloids for applications in coating and functional films [2, 4]

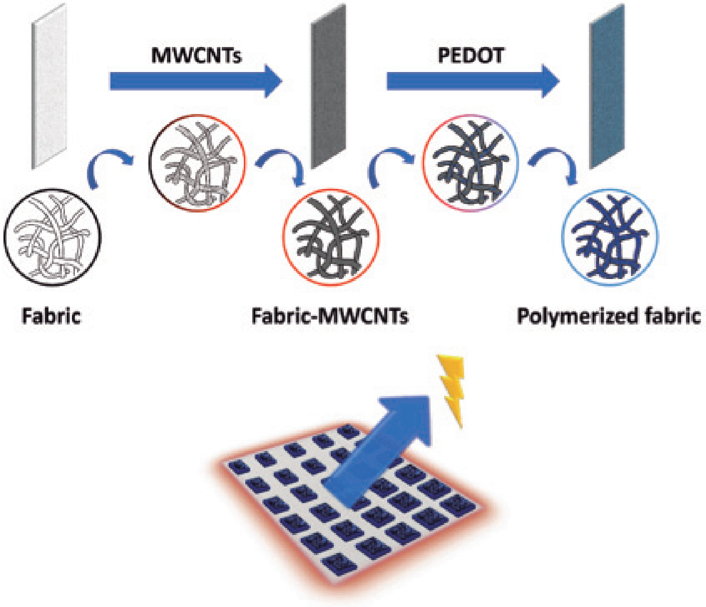

Figure 1 Schematic representation of the preparation of poly-3,4 ethylendioxythiophen (PEDOT) by electrochemical deposition on fabric substrates coated with carbon nanotubes through layer-by-layer (LbL).Reproduced with permission from ref. [3]. Copyright 2020, American Chemical Society.

Services to companies and other institutions

- Technical and scientific consulting services
- Synthesis and characterization of polymers on demand
- Design of new materials adapted to specific needs
- Feasibility studies for the use of novel materials to specific applications

Education and training

- Specialized training on polymer materials and their synthesis and characterization
- Specialized training on characterization of nanomaterials
- Specialized training on colloid science and interfaces

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MAX PLANCK PARTNER GROUP ON COLLOIDAL METHODS FOR MULTIFUNCTIONAL MATERIALS (CM3-LAB)

Rafael Muñoz-Espí, Clara M. Gómez, Francisco F. Pérez-Pla

Max Planck Partner Group on
Colloidal Methods for
Multifunctional Materials
(CM³-Lab)

The Laboratory of Colloidal Methods for Multifunctional Materials (CM3-Lab) is a Max Planck Partner Group of the Department of Physical Chemistry of Polymers of the Max Planck Institute for Polymer Research, based at the Institute of Materials Science of the University of Valencia (ICMUV). This cooperative project is funded by the Max Planck Partner Group Program of the Max Planck Society. The CM3-Lab is associated to the Unit of Polymer Materials at ICMUV.

The CM3-Lab focuses on the development of multifunctional hybrid systems to be used as platforms for the sustainable use of resources. How to apply the confinement provided by colloidal systems for the control of structure and properties of polymer materials and polymer/inorganic hybrids is the central scientific question. Colloidal synthetic routes involving heterophase systems are very versatile in the preparation of polymer/inorganic hybrid nanoparticles and nanocapsules [1]. Especially interesting are those materials derived from the covalent incorporation of functionalized inorganic building blocks into a polymer matrix through copolymerization with suitable monomers. The variability of the starting building blocks in terms of chemical nature and structure allows a fine tuning of the targeted features.

Nanocontainers produced by colloidal methods are able to protect the encapsulated materials from the external medium and, if required, to deliver them into a specific environment.

One possibility is to incorporate the inorganic component in polymer or polymer/inorganic hybrid colloids formed by miniemulsion polymerization. The encapsulation can also be combined with the in-situ surface deposition of further inorganic materials to generate multifunctional nanoparticles, as schematically shown in Figure 1 with an example. The interaction between the inorganic component and the surrounding polymer is shown to influence the final structure and the segregation of the inorganic components.

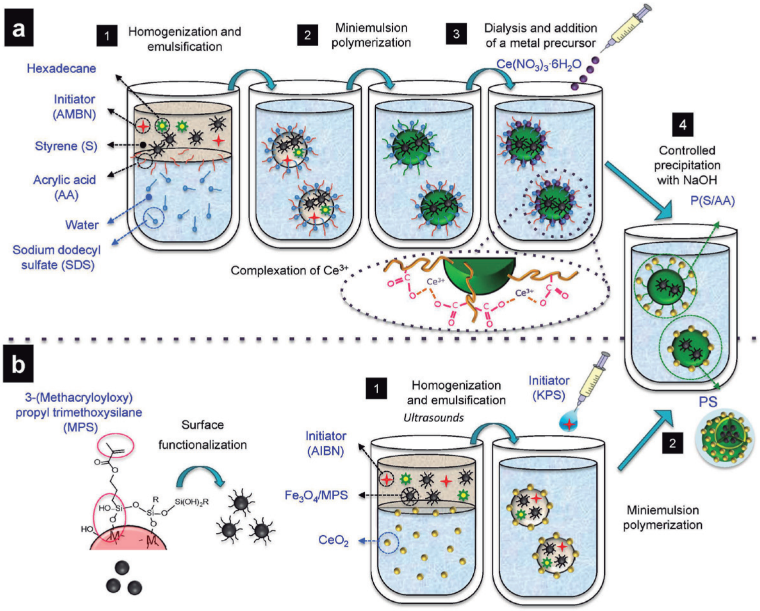

Figure 1 Schematic representation of the synthesis of magnetoresponsive multifunctional particles by (a) so-called Pickering miniemulsion polymerization and (b) in-situ crystallization. Reproduced with permission from ref. [2]. Copyright 2020, IOP.

Our team addresses the structure control in hybrid multicomponent nanomaterials and their potential applications, investigating thereby the following topics:

- Surface design and functionalization of nanoparticles for specific applications
- Effect of colloidal confinement in precipitation and crystallization processes, including the confinement on particle surface, in droplets and at droplet interfaces [3, 4]
- Catalytically active nanoparticles prepared by colloidal methods [2,3]
- Chiral nanoparticles and application in asymmetric catalysis
- Thermal energy storage by micro- and nanoencapsulation of phase change materials (PCMs) in polymer-based nanoparti-

cles

- Interaction of polymers with inorganic matter and preparation of composite materials

Web site: https://www.uv.es/muesra

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SEMICONDUCTORS AND EXTREME CONDITIONS (SEC)

Daniel Errandonea, Chantal Ferrer Roca, Domingo Martinez Garcia, Julio Pellicer-Porres, David Santamaria-Perez, Alfredo Segura

High-pressure (HP) research has experienced a vast progress in the course of the last two decades. This is a consequence of the combined advancement in instrumentations and experimental techniques as well as in computer simulation methods. Under compression, materials usually undergo a reduction of interatomic distances, which induces important changes in their characteristics, including the vibrational, magnetic, electronic, and mechanical properties. In particular, upon compression, atomic reorganization may be favored therefore inducing phase transitions between different crystal structures. New properties have been achieved, including high-temperature superconductivity and topological quantum phase transitions. In addition, novel materials with tailored properties for technological applications have been synthesized. High-pressure studies are also crucial for understanding the interior of planets.

In order to achieve high-pressure conditions, microscopic samples are compressed in a device known as diamond anvil cell, which enables the compression of a micron-sized piece of material to extreme pressures, typically up to around 200 gigapascals (two millions of atmospheres). Characterizing properties of materials under such conditions is a challenging task. At the SEC group, we combine several state-of the-art experimental techniques interpreting the results of experiments using accurate theoretical calculations.

In the last years, we have deepened into the knowledge of the properties of many different semiconductors, characterized the behaviour of ultra-incompressible materials, synthesized novel dense materials, recognized structural systematics of minerals, studied the CO2 chemistry in different environments and thermodynamic conditions, contributed to the developing of green technologies by studying barocaloric and photocatalytic materials, and determined the melting curves and pressure-temperature phase diagram of many elements of the Periodic Table, among other achievements. One of the last accomplishments is the determination of the P-T phase diagram of Niobium (Nb) [1] a step forward toward understanding the fusion of metals under extreme conditions. Figure 1 shows a schematic representation of the phase diagram determined for Nb.

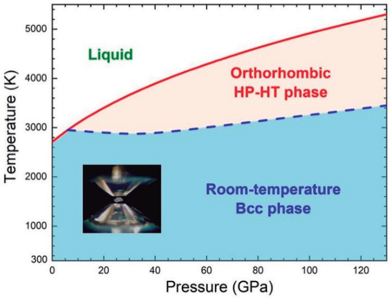

Figure 1 Pressure-Temperature phase diagram of Niobium determined by combining high-pressure synchrotron x-ray diffraction experiments and computing simulations. The red line is the melting curve and the blue dashed line the solid-solid phase boundary.

Our laboratory offers two complementary HP techniques: diamond-anvil cells and large-volume presses. As characterization techniques we use in our Lab optical-absorption measurements, Raman and infrared spectroscopy, laser-heating, and resistivity and Hall-effect measurements. We also visit in a regular basis large synchrotron facilities in order to perform, x-ray diffraction, infrared spectroscopy, and x-ray absorption measurements. As part of the Matter at High Pressure (MALTA) initiative we have access to additional techniques in other laboratories of Spain and got support from colleagues carrying out density-functional theory computing simulations. In summary, to understand high-pressure phenomena, we use an integrated approach, integrating multiple techniques, which has a power far greater than the sum of individual techniques. This has allowed us to precisely characterize the existence of phase transitions driven by pressure and to determine the crystal structure of the HP phase as well as the changes produced in symmetry and polyhedral coordination [2, 3]. A schematic representation of it is shown in Fig. 2. Other important results (but not all) are: a) the discovery of a novel dense silicate-carbonate phase at Earth's mantle pressure-temperature conditions [4]; b) the accurate characterization of the pressure dependence of Raman-active modes of hexagonal boron nitride [5]; and c) the understanding of changes induced by pressure in electronic and optical properties of vanadates [6].

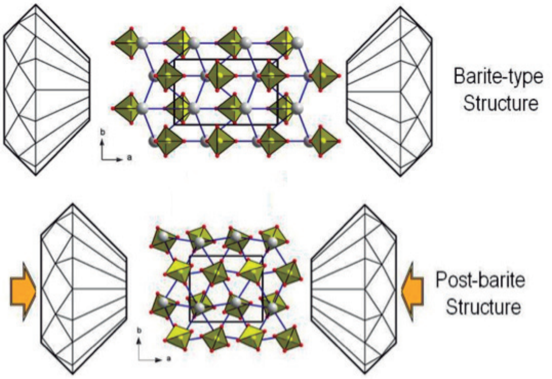

Figure 2 Schematic representation of the changes induced under compression in the crystal structure of Barite-type oxides. HP induces a phase transition modifying the symmetry of the crystal structure and increasing the packing efficiency

These studies are carried out with the financial support of the projects PROMETEO2018/123 EFIMAT from Generalitat Valenciana, PID2019-106383GB-C41, PGC2018-097520-A-I00 and RED2018-102612-T, funded the Spanish MICINN and FEDER. D.S.-P. acknowledges support from RyC-2014-15643.

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The Unit of Materials and Optoelectronic Devices (UMDO)

Juan P. Martínez Pastor

UMDO was born within the ICMUV in 1999 and led by Prof. Juan P. Martínez-Pastor. Our primary expertise lies in the field of Semiconductor Physics, particularly optical properties and exciton recombination dynamics in low dimensional semiconductors or artificial semiconductor hete-rostructures and nanostructures (quantum wells, wires and dots) based on III-V semiconductors and other compounds since 1990. This research line continues nowadays focused on quantum light produced by quantum dot semiconductors and its management for quantum communications.

After 2006 several research lines were opened in nanoscience and nanotechnology regarding the development of several types of nanomaterials (metal and quantum dots, multi-functional nanocomposites) and applications to photonics and plasmonics. In the last three years, we focused in linear and nonlinear optical properties, exciton recombination dynamics and applications in photonics of metal halide perovskite semiconductors. During the last 20 years of work fifteen PhD projects have been carried out in our labs within these subjects. Figures 1-3 show very recent examples of such studies and applications using lead halide perovskite nanocrystals.

In UMDO we collaborate with Dr. Albert Ferrando Cogollos, Full Professor at the Department of Optics (Faculty of Physics) and Dr. Isaac Suárez Álvarez, Assistant Professor at the Departament of Electronics Engineering (ETSE), in the field of nonlinear optical properties and applications in Photonics-Plasmonics, respectively. Other researchers are contributing to the achievements of UMDO within different projects, as Dr. Vladimir Chirvony (Senior researcher and old member of the Academy of Sciences of Belorussia). UMDO has set up along these years several research laboratories: Lab of Optical Spectroscopy for Nanosciences (1999), Lab of Nanomaterials and Nanotechnology (2006), Photonics Lab (2010), which are the base of the research developed until now.

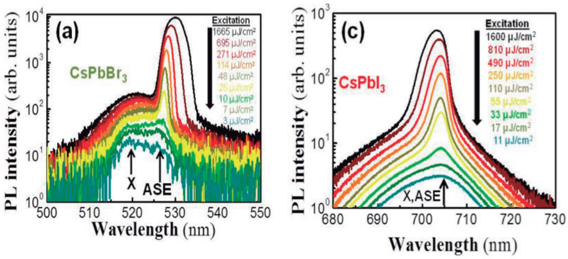


Figure 1. Amplification of the spontaneous emission (ASE) in films made of perovskite nanocrystals. The origin of ASE is the exciton radiative recombination.

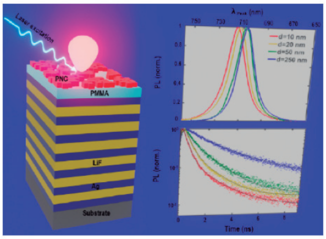


Figure 2. Purcell effect (enhancement of the exciton radiative rate) on light emitted by perovskite nanocrystals coupled to hyperbolic metamaterials consisting in a metal (Ag) and dielectric (LiF) multilayer.

See more information about the research lines in www.uv.es/umdo and related publications in the researchgate and Google Scholar links:

https://www.researchgate.net/profile/J_Martinez-Pastorhttps://scholar.google.com/citations?hl=es&user=kZhHGuMAAAAJ

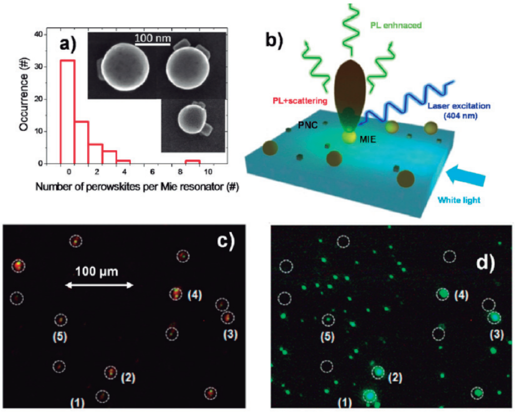


Figure 3. Samples containing TiO2 nanospheres (Mie resonators) with attached CsPbBr3 perovskite nanocrystals. Their coupling leads to enhancement of light emission and absorption.

The research in UMDO was possible through different projects led by Prof. Martínez-Pastor in the last few years:

- PROMETEOII/2014/059 (2014-2017) from GVA: Nanotecnología y Nanomateriales para Fotónica y Optoelectrónica (NANOFOT).
- TEC2014-53727-C2-1-R (2015-2017) from MINECO: Dispositivos optoelectronicos y fotonicos basados en nanomateriales avanzados: desde nuevos conceptos de nanofotonica hasta procesos y dispositivos "verdes" (OPTONANO).
- TEC2017-86102-C2-1-R (2018-2021) from MCINN: Dispositivos activos fotónicos basados en nanoestructuras semiconductoras tipo perovskita y metamateriales hiperbólicos (LNL-PHOTON).
- FET OPEN PROJECT (2019-2022) from H2020 program under contract no. 862656: DRop-on demand flexible Optoelectronics & Photovoltaics by means of Lead-Free halide perovskITes (DROP-IT).

LOW-DIMENSIONAL MATERIALS RESEARCH (LOWDIM)

Juan F. Sánchez-Royo

Our research develops within fields of **Nanophysics** and **Nanomaterials**, as we explore the physical properties of low dimensional materials with important electron confinement effects, at least in one of the three dimensions. In these materials, spatial constraints give rise to quantum size effects, which can significantly alter their electronic properties and deeply modify their behavior, as compared to their bulk counterparts. Those systems have shown a kaleidoscope of intriguing phenomena and extraordinary electronic, conducting, optical, thermal, mechanical and chemical properties, which may result in their use in wide range of nanotechnology. Technologically relevant examples of low-dimensional systems are two-dimensional (2D) materials, such as graphene, layered semiconductors and insulators, topological insulators, etc.

The primary goals of **LowDim** are the synthesis of novel 2D materials and the fundamental understanding of their properties. Current work-areas of the Unit include: (i) The development of preparation techniques which may produce large-area crystalline 2D layered materials exhibiting tunable band gaps, (ii) The development of doping techniques able to tailor the electronic, optical, and transport properties of 2D layered materials, (iii) The electronic and optical characterization of 2D materials and related devices, (iv) The development of structures based on 2D materials for optoelectronic applications, and (v) The design, development, and characterization of devices combining 2D materials, or other low-dimensional materials. LowDim is setting up its new Lab of Photoemission-ARPES (2020) and uses other common facilities of UMDO.

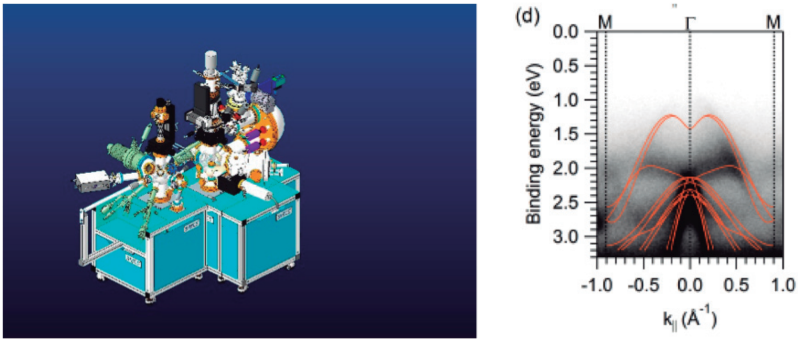


Figure 1. Left: Illustration of the Equipment recently installed in the labs of the group to perform ARPES and XPS measurements with spin discrimination. Right: Band dispersion of InSe measured by ARPES along the ΓM symmetry direction.

Until now, two PhD works have been developed in the context of this research line, these made by Mauro Brotons-Gisbert (2017) and Daniel Andrés Penares (2019). A third PhD work, by Rodolfo E. Canet Albiach is under progress. At the beginning of 2019, Dr. Marie Krečmarová, incorporated to the Lowdim research line, as a Postdoc contract under the EU project S2QUIP of the QUANTUM Flaghsip. Also, since 2019, the group has established an close collaboration with Professor Maria Carmen Asensio, from the Materials Science Institute of Madrid (ICMM) of the CSIC, creating an Associated Unity ICMM-CSIC/UVEG for the preparation and electronic characterization by photoemission of intelligent materials for energetic applications. More information about this research line and publications is given in

https://www.uv.es/lowdim/.

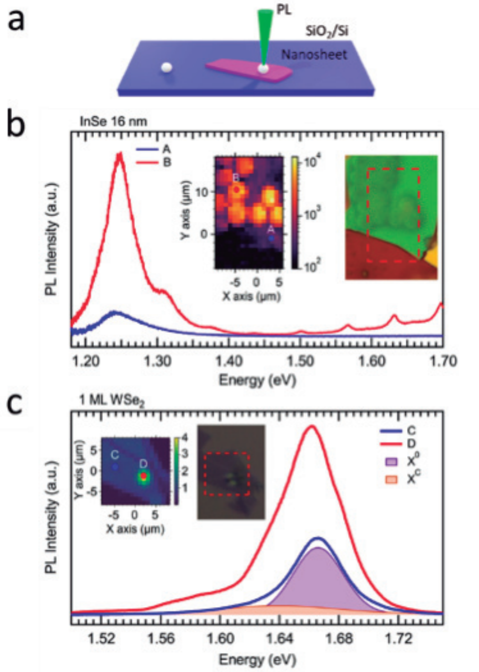


Figure 2. (a) Illustration of a 2D nanosheet partly covered by dielectric microspheres. (b)-(c) Effects of the microsphere on the photoluminescent response of InSe nanosheets and monolayer WSe2, respectively.

Metal-Halide Perovskites for Optoelectronics (MHPO)

Pablo P. Boix

The current energetic global system is not sustainable. The extensive use of fossil fuel is increasing the ambient pollution, and their influence on the green-house effect is reaching a point of no return. In order to generate future society solutions to save and generate energy, a technology which is economically sustainable and technologically versatile is required. In 2012, metal-halide perovskites arose as wonder materials. These semiconductors have originated revolutionary solar cells due to their high extinction coefficient, large charge-carrier diffusion length and optoelectric tunability, along with a potentially low-cost fabrication. These materials adaptability is embodied by the variety of forms they can adopt, including 2D or quasi-2D structures and nanoparticles among others (Figure 1). Their outstanding properties transcend photovoltaic applications, and place metal halide perovskites as excellent candidates for next generation light-emission, detection or even computational technologies.

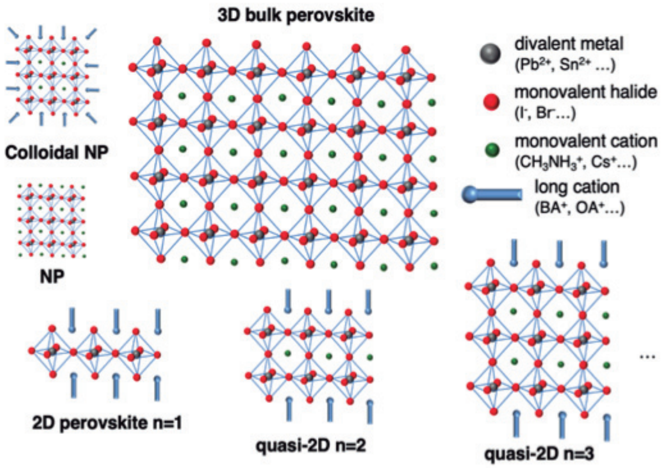


Figure 1. Compositional and morphological examples in the metal-halide family.

Our work focuses on the characterization and modelling of the main physical processes determining perovskite-based devices' performance as an initial step to propose solutions to reach their theoretical limit. In this line, the MHPO group is setting up a complete Lab of Optoelectronic Devices and uses other common facilities of UMDO, as some specific optical-based techniques, such as time resolved photoluminescence. In combination with the structural characterization tools at the institute, we can tackle the whole material-to-device development range.

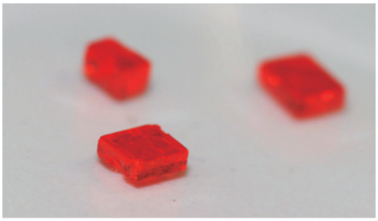


Figure 2. $CH_3NH_3PbBr_3$ single crystal fabricated from solution method.

From that perspective, we intend to benefit from the flexibility of this family of materials to take perovskite optoelectronics to the next level. Top-down approaches, which take monocrystalline structures as the starting point (Figure 2), are combined with bottom-up strategies such as the implementation of perovskite nanoparticles.

These studies are partially funded by the projects SEJI/2017/012 by Generalitat Valenciana and MAT-2017-88905-P by the Spanish MICINN and FEDER funds. See more information about this research line and related publications in the Publons and Google Scholar links:

https://publons.com/researcher/1618696/pablo-p-boix/

https://scholar.google.com/citations?hl=es&user=VNIwSaUAAAAJ

THEORY AND SIMULATION OF QUANTUM MATERIALS (QMAT-SIM)

Alejandro Molina-Sánchez, Alberto García-Cristóbal

We investigate optics, magnetism, in quantum materials with focus on 2D materials such as graphene, hexagonal boron nitride, transition metal dichalcogenides, or chromium trihalides. Nowadays, the family of 2D materials (Figure 1) displays a broad range of electronic properties and contains metals, semiconductors, ferromagnets, and superconductors. Graphene is probably the most famous 2D material, but it is a semi-metal and it lacks from the electronic bandgap fundamental for many applications. In the last years, 2D materials are complementing or substituting graphene in many applications, and new 2D materials are appearing with novel properties like 2D ferromagnetism, topological semimetals and Mott insulators.

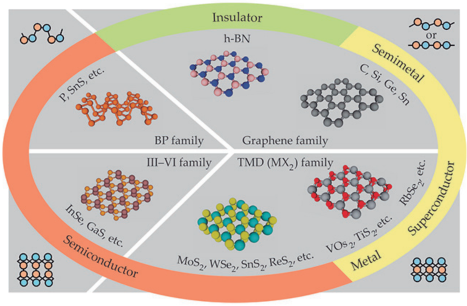
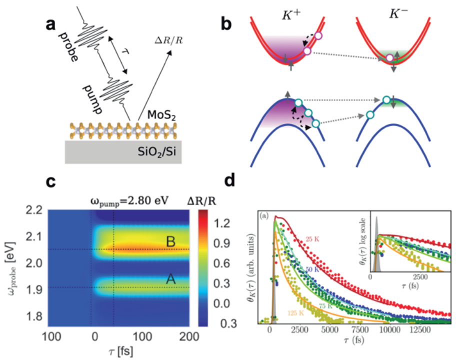


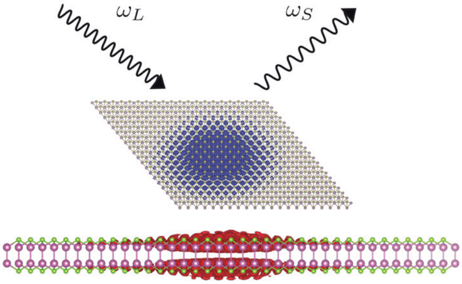
Figure 1. Classification of the main 2D materials. Extracted from Physics Today 69, 38 (2016)



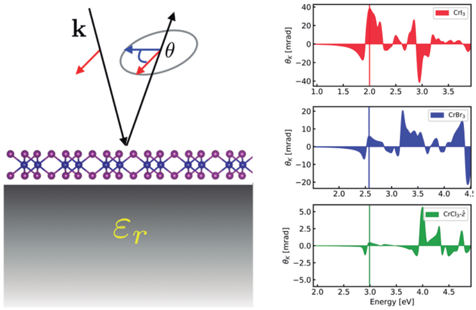
We apply theoretical solid-state physics and ab initio methods to the following research:

- **Many-body effects in the optical properties** (Figure 2).

Topics involve: electronic structure, excitons, electron-phonon interaction by using Raman spectroscopy, interlayer excitons in 2D heterostructures



- **Out of equilibrium properties** (Figure 3). Topics involve: ultrafast optical spectroscopy, carrier dynamics, spin and valley polarization dynamics, exciton generation and magnetization dynamics.



- **Magnetism in 2D materials** (Figure 4). Topics involve: Kerr spectroscopy, magnetic anisotropy and strong electronic correlations.

The simulations are performed in the high-performance computer centers of the University of Valencia (Tirant), Barcelona Supercomputing Center (BSC – Mare Nostrum), and, in a Super-Micro cluster hosted at ICMUV.

The research has the financial support of the Ramón y Cajal Grant and Juan de la Cierva Grant from the Spanish MINECO, and project FAST-2DMAT funded by the Luxembourg National Research fund. See more information about this research in

https://sites.google.com/view/2dmat-sim

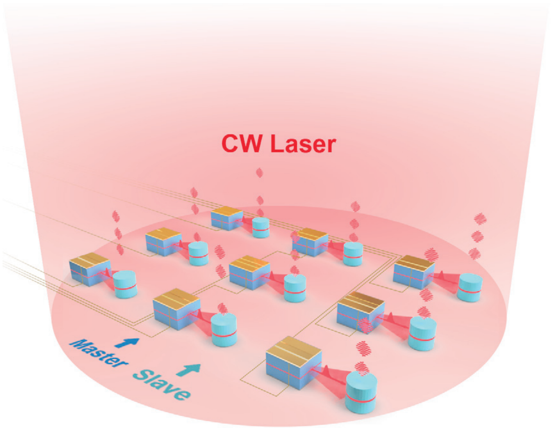
And related publications in Google Scholar:
https://scholar.google.com/citations?hl=es&user=MRLOVbQAAAAJ

SEMICONDUCTOR ARTIFICIAL QUANTUM SYSTEMS (SAQS)

Guillermo Muñoz Matutano

The recent development of nanoscience and nanotechnology is pushing the market to include new nano-inspired devices, sensors and tools. In many cases, quantum properties of light and matter at the nanoscale are responsible for their unique nano- and meso-scaled mechanisms and behaviours. The development of new applications and devices depends to a large extent on the control and manipulation of these artificial quantum systems.

At present, there is a large variety of artificial **atom platforms**, including, single semiconductor quantum dots (Figure 1), non-linear materials, 2D exfoliated semiconductors, nitrogen vacancy centres in diamond, plasmonics devices or exciton polaritons, among others. Due to their exceptionally high single-photon purity and indistinguishability, solutions where single semiconductor nanostructures act as the active material in the device deserve much of the attention. The success of these research strategies will provide light matter-based quantum devices in the future, like high repetition rate single-photon emitters, Fock state optical switchers, all-optical gates, or light-based 2D driven dissipative quantum simulators,.



In that direction, the different quantum blockade effects studied in semiconductor nanostructure platforms are successful examples. In this blockade scenario, due to the discreteness nature of the particle under study, the presence of a first particle in the device will block the transmission of a second particle through the same device. This is the case of the Coulomb and the Spin Blockade in semiconductor Quantum Dots or the Photon Blockade in semiconductor cavity QED platforms. Both are the principal mechanisms to produce new devices operating in the single quantum particle picture (electrons, spins, photons, …), and hence being the principal mechanisms to offer semiconductor devices for single photon and entangled photon emission, quantum gating and single particle transistors, quantum cryptography and computation schemes or quantum sensing applications.

Among all light-matter interaction physical schemes, **Quantum Polaritonics with 2D semiconductors** is an emerging field that has the potential to add a number of features to the standard quantum technologies toolbox. Exciton-polaritons are half-matter, half-light quasiparticles that form in semiconductors when an exciton interacts sufficiently strong with light. Exciton-polaritons in semiconductor microcavities have revealed themselves as one of the richest realizations of a light-based quantum fluid. In the regime of large two-body interactions, **polaritons can be used to manipulate the quantum properties of a light field** (Nature Materials 18, 213 (2019)). Further progress in this direction will open up exciting experiments for the realization of new quantum semiconductor on-chip devices, and future light-matter quantum simulation platforms. For this, SAQS is setting up his own Lab extending some of the capabilities of the "Lab of Optical Spectroscopy for Nanosciences" from UMDO.

The actual research line has financial support from the project "Two-Dimensional Semiconductor Photonic Dots (2D-SPD)" (RTI2018-099015-J-I00) funded by the Ministry of Science, Innovation and Universities, the State Research Agency (AEI) and the European Regional Development Fund (FEDER).

See more information about this research line and related publications in the researchgate and Google Academics links:

https://www.researchgate.net/profile/Guillermo_Munoz-Matutano

https://scholar.google.com/citations?hl=es&user=iCLxx_IAAAAJ

CHEMISTRY OF ADVANCED MATERIALS FOR OPTOELECTRONICS DEVICES (CHEMDO)

Rafael Abargues

Energy transitions are ongoing processes all over the world. How to design pathways towards sustainable energy transition has attracted worldwide concerns. Understanding the possible transition pathways of the energy system requires the integration of new energy technologies, environmental sciences, economics, and management.

Nanoscience has a key role in the coming sustainable energy transition. The design and development of advanced nanomaterials to improve the different energy conversion and storage systems, as well as environmental issues, have shown exciting results and a promising future. One exciting aspect of nanotechnology concerns nanomaterials' formation on a substrate as thin films (Figure 1) to fabricate new solid-state devices involving photovoltaics, optoelectronics, thermoelectrics, electrocatalysis and sensing. Among the different strategies to approach advanced materials, solution-processed nanomaterials are very promising for the low-cost manufacturing of the next generation of high-performance micro and nanodevices in a solid-state.

This research line concerns mainly the implementation through a deep fundamental understanding of the chemistry of solid-state functional materials for advanced technological needs by solution-processed methods. At CHEMDO, we have broad expertise on the synthesis of a wide range of nanomaterials based on conducting polymers, transition metal oxides, noble metal nanoparticles, quantum dots, metal halide perovskite nanocrystals, and their nanocomposites. We formulate our nanomaterials as inks to be coated by solution-processed methods. Most of these materials are in-situ synthesized after deposition with outstanding properties, allowing us to fabricate both small and large area devices by using direct printing deposition techniques. For this, CHEMDO has its own Chemistry Lab and uses other facilities from UMDO, as some installed at the Lab of Nanomaterials and Nanotechnology.

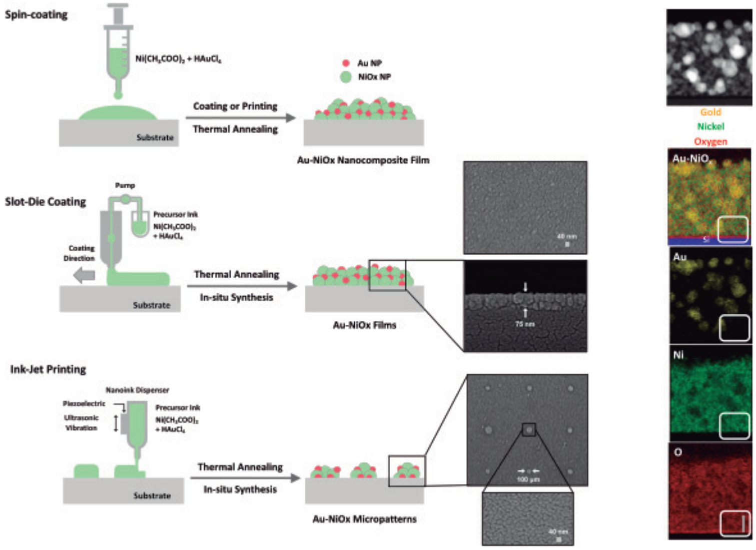


Figure 1. Printing of nanomaterials and TEM characterization

Our materials have already shown very promising properties for energy generation (photovoltaics and thermoelectrics), energy storage (H2 generation from water splitting), solar harvesting functions (photocatalysis) and sensing (food safety monitoring and explosive sensors).

https://scholar.google.es/citations?user=632SsTEAAAAJ&hl=es

https://www.researchgate.net/profile/Rafael_Abargues_Lopez

LABORATORY OF FIBER OPTICS (LFO)

Miguel V. Andrés, José Luis Cruz, Antonio Díez, Enrique Silvestre, Martina Delgado-Pinar, Abraham Loredo-Trejo, Luis A. Sánchez

The research activity of the Laboratory of Fiber Optics (LFO) follows two main lines. On the one hand, we contribute to the development of optical fiber technologies to make available special fibers and fiber components with specific properties. On the other hand, we pay attention to particular applications. The research topics in which we are interested are the development of fiber lasers, novel fiber light sources, and photonic biosensors, by exploiting the properties of in-fiber acousto-optics, high Q whispering gallery modes resonators, photonic crystal fibers, tapered fibers, and special fiber gratings.

In parallel with our experimental work, we have also a significant theoretical activity that includes the development of new theoretical tools for the study on light propagation in both linear and nonlinear regimes, and the design of waveguides and optical fibers with specific properties.

Most of our research projects exploit the fabrication facilities that we have developed along the years. We have built a pulling tower for the fabrication of silica photonic crystal fibers (Fig. 1), a tapering rig for the preparation of tapered fibers, microfibers and microcapillaries (Fig. 2), and a UV laser equipment for the photo-inscription of in-fiber gratings (Fig. 3).

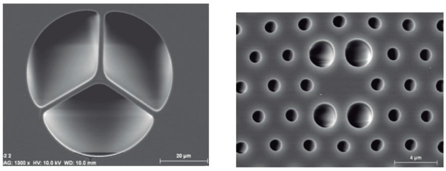


Fig. 1. Special photonic crystal fibers: (left) suspended core, and (right) polarization maintaining fibers.

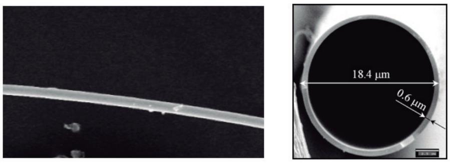


Fig. 2. Submicrometric microfiber (left), and microcapilary with submicrometric wall thickness (right).

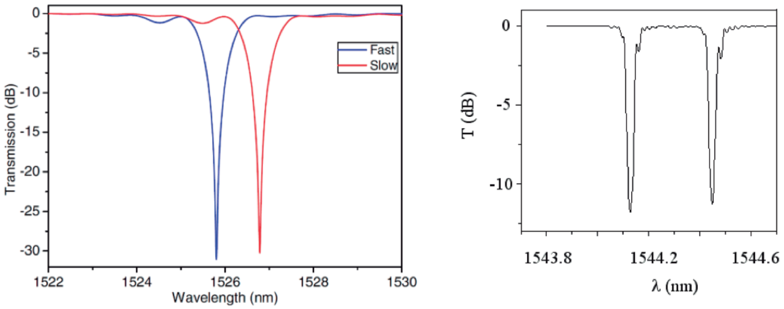


Fig. 3. A long period grating with subnanometric linewidth (left), and two superimposed Bragg gratings with 40 pm linewidth (right).

For example, the combination of fiber lasers, nonlinear photonic crystal fibers with specific chromatic dispersion, and acousto-optic fiber devices enables the design and fabrication of special fiber light sources. Figure 4 shows two examples of our results: a laser that emits a vector beam with radial polarization by exploiting the in-fiber acousto-optic interaction, and a light source with tunable emission wavelengths based on polarization modulation instability (PMI) in a nonlinear photonic crystal fiber (PCF).

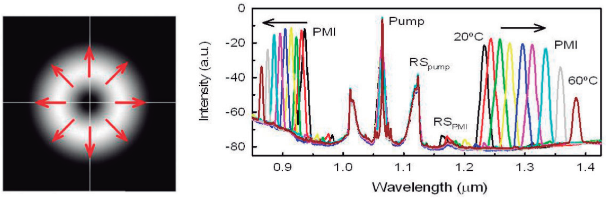


Fig. 4. Vector beam image produced by a fiber laser (left), and wavelength tunable light source based on PMI produced in on a nonlinear PCF (right).

In the last years we have proposed several original fiber characterization techniques based on measuring the resonances of the azimuthal surface waves, i. e., the so-called whispering gallery modes, which are excited on the fiber itself. Thus, we have been able to perform a fine characterization of thermal effects in fiber Bragg gratings and doped fibers by measuring ultra-small temperature changes in the fiber; and we have developed a novel approach for the measuring of fiber strain-optic coefficients (Fig. 5). In-fiber acousto-optics is being exploited as well in our laboratory for the characterization of optical fibers as, for example, the measurement of the nonlinear refractive index coefficient using very short samples of optical fibers.

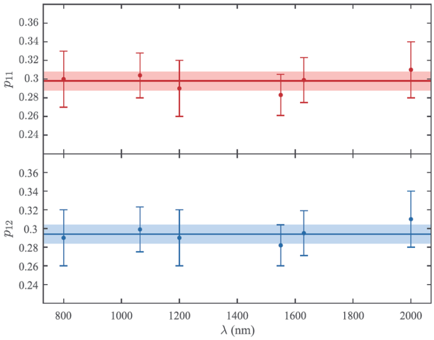


Fig. 5. Measurement of the strain-optic coefficients of PMMA from 800 to 2000 nm

Recently, we have started several projects focused on the development of photonic biosensors using fiber technologies. Figure 6 gives two examples in which we show the potential of fiber technologies for the development of new concepts in biosensing.

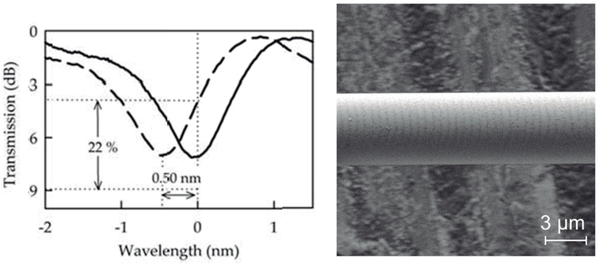


Fig. 6. Wavelength shift of a long period grating resonance with narrow linewidth in a biosensor application (left), and biograting written onto a microfiber with strong evanescent fields (right).

You can find more details on our research activity and publications in our web page: www.uv.es/lfo. Follow us at @LFO_UV in Twitter to be up to date of our activities!

At the present we are carrying out four projects:

- (2019-2022) Optical Fibers and Signal Processing (FOPS, Ref.: PROMETEO-2019-048), Generalitat Valenciana.

- (2020-2024) Integrated Photonics-Nano Technologies for Bioapplications (IPN-Bio, Ref.: H2020-MSCA-RISE-872049), European Commission.

- (2020-2023) Acoustic Waves in Optical Fibers and Microcavities (AWOFM, Ref.: PID2019-104276RB-I00), Ministerio de Ciencia e Innovación – Fondo Europeo de Desarrollo Regional (FEDER).

- 2020-2021), New ultrafast spectroscopy techniques (Ref.: IDIFEDER-2020-064), Generalitat Valenciana.

25 YEARS OF MATERIALS SCIENCE WORKSHOP

INVITED PRESENTATIONS

DIAGNOSTICS OF COVID-19 AND THE EMERGENCE OF NEW TECHNOLOGIES AND MATERIALS

Laura M. Lechuga

Nanobiosensors and Bioanalytical Applications Group. Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC, BIST and CIBER-BBN. Campus UAB, Bellaterra, 08193 Barcelona, Spain

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Point-of-care (POC) biosensor devices have experienced an intense development for years, but the translation to commercial products widely adopted in the diagnostics field have been restricted to few successful examples, as the glucose biosensor or the pregnancy test. There are several reasons, both technical and market barriers, for such slow translation. However, COVID-19 pandemic has evidenced how useful POC technologies could become when massive diagnostics is required for millions of users in a frequent way.

The dramatic spread of COVID-19 pandemics is forcing the urgent development of novel POC diagnostic tools for the rapid testing and screening of the population with sufficient sensitivity and specificity levels. In fact, reliable and early diagnostics of COVID-19 has become one of the major challenges in the correct management of the Pandemic. Current diagnostic techniques rely on polymerase chain reaction (PCR) tests, which provide the required sensitivity and specificity. However, its relatively long time-to-result, and the need of specialized laboratories, delays overly the massive detection.

Strong efforts are being pursuing at worldwide level to surpass this bottleneck by offering reliable, fast and user-friendly diagnostics tests based on emerging technologies (as photonics biosensors) and materials. In this effort, CoNVat project is one of the first projects funded by the H2020 European Union Framework program to fight against COVID-19. Main objective is to deliver a Point-of-Care (POC) Nanophotonics Biosensor platform capable to provide an accurate and fast SARS-CoV-2 coronavirus detection (less than 30 minutes), without requiring complex equipment and directly from the human sample.

THE EUROPEAN XFEL: NEW SCIENCE OPPORTUNITIES, START OF USER OPERATION AND FIRST RESULTS.

Sakura Pascarelli

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In the past decade we have seen very important developments in the field of accelerator based X-ray user facilities, with the advent of 4th generation synchrotron sources and MHz rate free electron lasers. The first hard X-ray free-electron laser, LCLS (US) became operational in 2009 and over the last decade four additional hard X-ray FELs have begun user operation - SACLA (Japan), PAL-FEL (Korea), Eu-XFEL (Germany) and SwissFEL (Switzerland). Among these, the Eu-XFEL is the first hard XFEL powered by a superconducting linear accelerator, which enables MHz rate pulse generation. A specificity of XFELs is their very short pulse duration (10-100fs) opening new scientific opportunities to probe matter at the atomic scale, with chemical selectivity and bulk sensitivity, and on the relevant timescales. Ultrashort, high intensity X-ray pulses from FELs are also providing a totally new approach to structural determination with X-rays, where useful structural information from very small, “radiation sensitive” or “dynamic” crystals is acquired before radiation damage sets in. After many years of construction, user operation at the Eu-XFEL has finally begun. In the Fall of 2017, two hard X-ray instruments FXE (devoted to studying extremely fast processes) and SPB/SFX (for investigating biomolecules and biological samples) opened to external users. Before the end of 2018, the two soft X- ray instruments SQS (Small Quantum Systems) and SCS (Spectroscopy and Coherent Scattering) followed. Finally, two additional hard X-ray instruments are presently welcoming first user groups: HED for studying matter under extreme pressures and temperatures, and MID for investigating nanostructures or irregularly ordered materials such as glass, liquids and biological substances. In this talk I will first briefly introduce the present performance of the facility in terms of electron and photon beam characteristics and operation modes. I will then report first results from early user experiments, and comment on some important challenges ahead.

NOVEL ANALYTICAL CHROMATOGRAPHY-MASS SPECTROMETRIC PROCEDURES IN ART AND ARCHAEOLOGY

Maria Perla Colombini

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Since ancient times, a wide variety of natural organic materials have been used as adhesives, sealants, painting and coating materials. Proteins, oils, gums, natural resins and resinous materials played a prominent role, since their intrinsic properties meant that they could be used not only as painting materials, adhesives, hydro-repellents, coating and sealing agents, but also as flavours, incense, ingredients for cosmetics, medicines and mummification balms. The chemical characterization of such organic materials when properly integrated with related information from historical sources and archaeological data, has in the last few years considerably improved our knowledge of painting techniques, crafts and technologies of the past, and has provided archaeologists with valuable information. In fact, identifying specific materials from molecular patterns helps in assessing the role that these substances played and in determining the use of artefacts on which these residues survive.

The characterization of organic materials is a challenge for a chemist, due not only to the complexity of the chemical composition of the natural substances that may be present alone and in mixtures, but also to changes in the chemical composition as a consequence of human activities. For instance, heating processes applied to plant resins deeply modified their chemical composition, inducing aromatisation, demethylation and decarboxylation reactions with formation of new species. Moreover, degradation due to ageing under the influence of different environmental circumstances or improper storage leads to further changes in the composition of the original materials.

The analytical procedures based on mass spectrometric techniques applied to artistic objects able to identify artistic/archaeological marterials and to study their degradation pathways are outlined. In particular, analytical pyrolysis (EGA-MS and Py-GC/MS), and chromatography/mass spectrometry (GC-MS and HPLC-MS) will be discussed highlighting their abilities in solving complex molecular mixtures and in achieving reliable results [1-3]. The identification at a molecular level of organic materials in heritage objects by using the above techniques, requires the collection of micro-samples followed by micro-destructive analysis, after specific sample pre-treatments. To overcome such a problem, in the last years the analysis of volatile organic compounds (VOCs) released by organic materials in heritage objects has been investigated: the ability of selected ion flow tube-mass spectrometry (SIFT-MS) is herein discussed as a non-invasive tool for VOCs profiling of natural and synthetic resins. SIFT-MS is a direct mass spectrometric technique, recently introduced as a portable device, which achieves quantitative analysis of VOCs at trace levels in real time, by applying precisely controlled ultra-soft chemical ionization using eight different chemical ionization agents, and, above all, avoiding any sampling step [4]. The figure summarizes the main information that we can obtain by using the mentioned analytical techniques. Examples of material identification and degradation studies of paintings and archaeological objects are presented by employing these analytical procedures.

The mass spectrometric approach

No sampling

SIFT-MS

real-time quantitative and qualitative analysis of VOCs in gas phase at trace levels emitted by heritage objects

No sampling

Analytical pyrolysis

EGA-MS, multishot Py-GC-MS selective study of the differents fractions evolved at differet temperature. Fingerprint of natural and synthetic organic materials at molecular level.

GC-MS

Identification of natural organic materials, alkyd resins and low molecular weight synthetic resins

HPLC-MS

Identification of proteins, lipids, additives, natural and synthetic dyes

[1] J. La Nasa, G. Biale, B. Ferriani, R. Trevisa, M.P. Colombini, F. Modugno, Plastics in Heritage Science: Analytical Pyrolysis Techniques Applied to Objects of Design. Molecules **25***, 1705 (2020). DOI: 10.3390/molecules25071705*

[2] I. Bonaduce, E: Ribechini, F. Modugno, M.P. Colombini, "Analytical Approaches Based on Gas Chromatography Mass Spectrometry (GC/MS) to Study Organic Materials in Artworks and Archaeological Objects" 291-327 (2017). In: Mazzeo R. (eds) Anal. Chemistry for Cultural Heritage. Topics in Current Chemistry Collections. Springer, Cham. DOI:10.1007/978-3-319-52804-5_9

[3] J La Nasa; F Modugno, I Degano, "Liquid chromatography and mass spectrometry for the analysis of acylglycerols in art and archeology", Mass Spectrometry Reviews, 00, 1–27 (2020). DOI: 10.1002/mas.21644

[4] J. La Nasa, F. Nardella, F. Modugno, M. P. Colombini, E. Ribechini, I. Degano, "SIFT-ing archaeological artifacts: selected ion flow tube-mass spectrometry as a new tool in archaeometry", Talanta, **207***, 120323 (2020). DOI: 10.1016/j.talanta.2019.120323*

GATED NANOMATERIALS FOR BIOMEDICAL APPLICATIONS

Ramón Martínez-Máñez [1,2,3,4*]

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In last years, nanomedicine and nanotherapy are gaining an increasing attention as alternative to conventional treatments in main pathologies which require a selective and controlled drug administration. Numerous nanocarriers with different characteristics have been designed and applied in drug delivery protocols. In this filed some delivery strategies are based on more sophisticated designs in which nanocarriers are tailored to deliver their cargo in the presence of certain stimuli. An attractive approach in this context is related with the preparation of "gated materials". Gated materials are predesigned to selectively deliver payloads on-command from a porous support in response to selected stimuli.[1] Among possible porous systems, mesoporous silica nanoparticles (MSNs) are perhaps the most widely used. MSNs present unique characteristics as high loading capacity, biocompatibility, chemical inertness and high surface area which can be easily functionalised using the well-known alkoysilane chemistries. In this talk new advances in the design of gated nanomaterials for sensing and drug delivery applications will be described.[2] Moreover, the talk will also describe some advances towards the design of nanobots using gated nanoparticle able to communicate each to another via the exchange of chemical messengers and have autonomous movement.[3]

[1] A. García-Fernández, E. Aznar, R. Martínez-Máñez, F. Sancenón. New Advances in In Vivo Applications of Gated Mesoporous Silica as Drug Delivery Nanocarriers. Small 2020, 16, 1902242. DOI: 10.1002/smll.201902242

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HYBRID FUNCTIONAL ORGANIC/INORGANIC NANOMATERIALS: DEVELOPMENT, CHARACTERIZATION AND APPLICATIONS

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We aim to present the development of hybrd functional organic/inorganic nanocarriers for biomedical applications, smart coatings, sensing and photocatalyis.

Organic/inorganic nanocapsules offer the versatility to cover a wide range of mesoscopic properties for sophisticated applications. By means of the miniemulsion process, we can design custom-made hybrid nanocapule systems for different purposes. The encapsulation and release of a great variety of payloads, ranging from hydrophobic to hydrophilic substances has been successfully achieved in a highly controlled manner and with an unmatched high encapsulation efficiency.

The preparation of organic/inorganic nanocontainers with a hydrophilic core from water-in-oil emulsions and their subsequent transfer to aqueous medium is of special importance since it enables the efficient encapsulation of hydrophilic payloads in large quantities. However, major challenges are associated with their synthesis include low colloidal stability, leakage of encapsulated payloads due to osmotic pressure, and a demanding transfer of the nanocontainers from apolar to aqueous media. We present a general approach for the synthesis of hybrid nanocontainers that are colloidally stable, not sensitive to osmotic pressure, and responsive to environmental stimuli that trigger release of the nanocontainer contents. Additionally, the nanocontainers can selectively deliver one or two different payloads. Our approach uniquely enables the synthesis of nanocontainers for applications in which aqueous environments are desired or inevitable.

THE ENERGY TRANSITION IN SPAIN (2020-2030)

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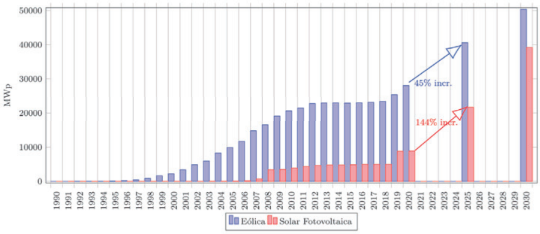
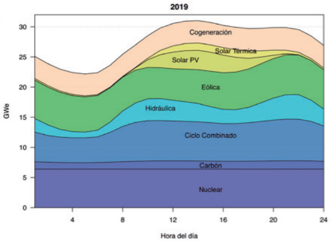
Among the largest regions of the world, Europe is probably the one that best exemplifies the adoption of energy and climate measures as recommended by the Paris 2016 Agreement on Climate Change. In this sense, every country of the EU had to elaborate a national energy and climate plan (2020-2030) that in Spain was called by the acronym PNIEC (Plan Nacional Integrado de Energía y Clima). According to this plan, the main target was to reduce emissions by 40% from 1990 levels.

A very significant aspect of the power electricity system is the daily pattern of the power demand, which for Spain is shown in the figure below and represents the hourly (0-24 h) average for all days of the year 2019. This curve shows a minimum of about 23 GW in the electricity demand at night and a maximum of about 31 GW around noon, which is much less that the total power capacity of the Spanish system (110 GW).

In this talk we would like to remark that 2019 has been an excellent year for reaching the PNIEC targets, since there has been a very large drop of coal generation passing from a 14.5% of the total electricity in 2018 to just 4.5% in 2019. This drop of 24.3 TWh also implies a downturn in emissions since the coal generation has been mainly substituted by gas combined cycle and solar plants.

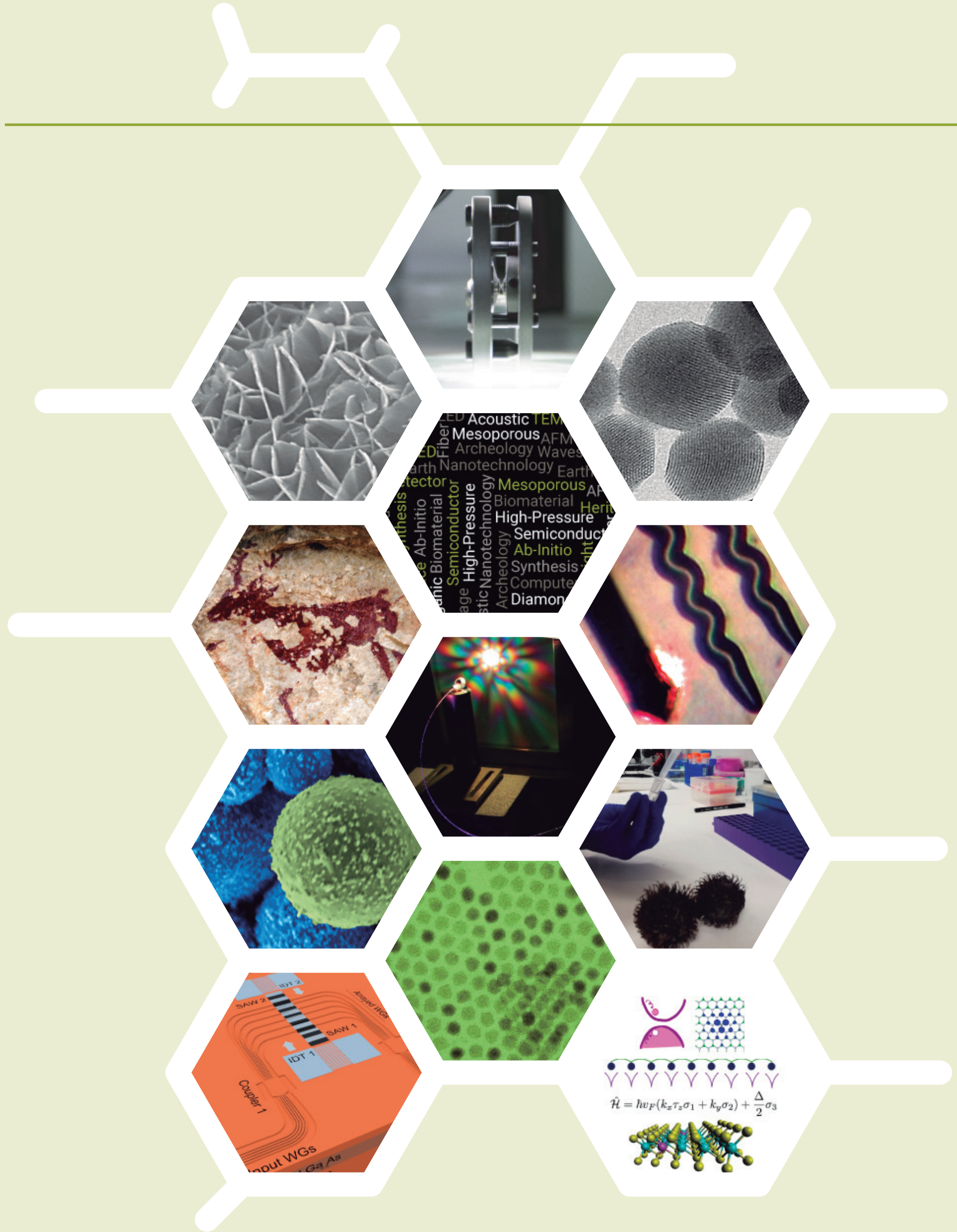
The PNIEC contemplates that our electricity system for 2030 will be highly based on electricity generation by renewable plants (see Figure below): 50.3 and 48.5 GW for wind and solar, respectively. This implies that every year in the period 2020-2030, some 5 GW between solar and wind will have to be implemented. It is therefore an excellent news that just only in 2019, solar plants with a total of about 4 GW were implemented.





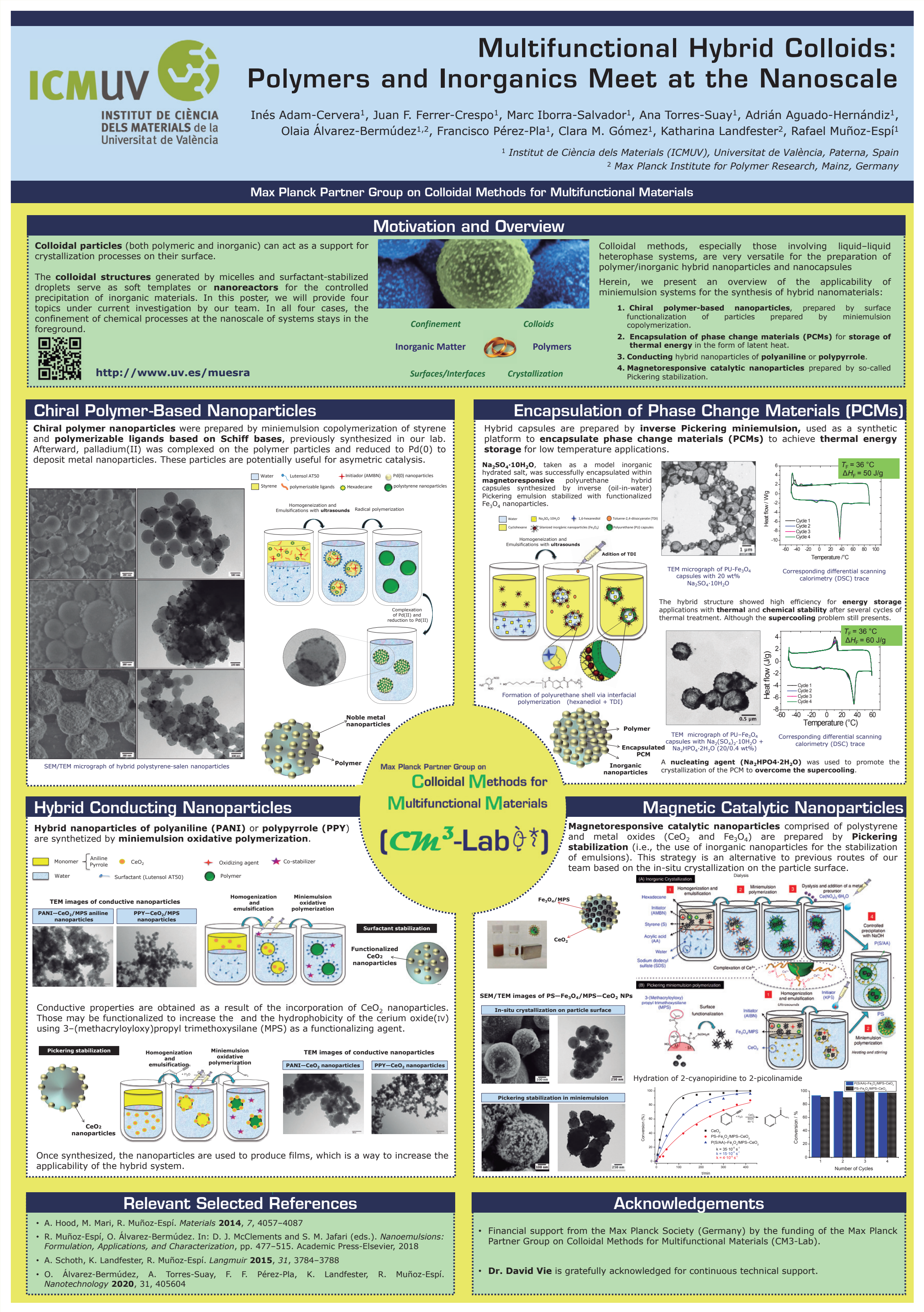
Since the major sources of electricity in 2030 will be solar and wind, which are non-dispatchable, it would be needed, in order to avoid curtailment, to store the energy surplus when the solar and wind are very intense, so that this energy could be used later as backup energy. Since the storage of energy equipment is relatively costly, it would be needed to undertake studies to choose the most proper utensils. In this talk we will focus mainly in hydro-pumping, electrochemical batteries and hydrogen.

Finally, by applying linear programming optimization techniques we have made optimal the large deployment of non-dispatchable variable renewable energies (VRES). By “optimal” we mean that the shares of VRES would simultaneously minimize both the backup and the surplus power components for the whole set of hours (8760) in the year.



25 YEARS OF MATERIALS SCIENCE WORKSHOP

POSTER PRESENTATIONS



Multifunctional Hybrid Colloids: Polymers and Inorganics Meet at the Nanoscale

Inés Adam-Cervera[1], Juan F. Ferrer-Crespo[1], Marc Iborra-Salvador[1], Ana Torres-Suay[1], Adrián Aguado-Hernándiz[1], Olaia Álvarez-Bermúdez[1,2], Francisco Pérez-Pla[1], Clara M. Gómez[1], Katharina Landfester[2], Rafael Muñoz-Espí[1]

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INSTITUT DE CIÈNCIA DELS MATERIALS de la Universitat de València

Max Planck Partner Group on Colloidal Methods for Multifunctional Materials

Motivation and Overview

Colloidal particles (both polymeric and inorganic) can act as a support for crystallization processes on their surface.

The **colloidal structures** generated by micelles and surfactant-stabilized droplets serve as soft templates or **nanoreactors** for the controlled precipitation of inorganic materials. In this poster, we will provide four topics under current investigation by our team. In all four cases, the confinement of chemical processes at the nanoscale of systems stays in the foreground.

http://www.uv.es/muesra

Colloidal methods, especially those involving liquid–liquid heterophase systems, are very versatile for the preparation of polymer/inorganic hybrid nanoparticles and nanocapsules

Herein, we present an overview of the applicability of miniemulsion systems for the synthesis of hybrid nanomaterials:

1. **Chiral polymer-based nanoparticles**, prepared by surface functionalization of particles prepared by miniemulsion copolymerization.
2. **Encapsulation of phase change materials (PCMs)** for **storage of thermal energy** in the form of latent heat.
3. **Conducting** hybrid nanoparticles of **polyaniline** or **polypyrrole**.
4. **Magnetoresponsive catalytic nanoparticles** prepared by so-called Pickering stabilization.

Chiral Polymer-Based Nanoparticles

Chiral polymer nanoparticles were prepared by miniemulsion copolymerization of styrene and **polymerizable ligands based on Schiff bases**, previously synthesized in our lab. Afterward, palladium(II) was complexed on the polymer particles and reduced to Pd(0) to deposit metal nanoparticles. These particles are potentially useful for asymetric catalysis.

SEM/TEM micrograph of hybrid polystyrene-salen nanoparticles

Encapsulation of Phase Change Materials (PCMs)

Hybrid capsules are prepared by **inverse Pickering miniemulsion,** used as a synthetic platform to **encapsulate phase change materials (PCMs)** to achieve **thermal energy storage** for low temperature applications.

$Na_2SO_4 \cdot 10H_2O$, taken as a model inorganic hydrated salt, was successfully encapsulated within **magnetoresponsive** polyurethane hybrid capsules synthesized by inverse (oil-in-water) Pickering emulsion stabilized with functionalized Fe_3O_4 nanoparticles.

Formation of polyurethane shell via interfacial polymerization (hexanediol + TDI)

TEM micrograph of PU-Fe_3O_4 capsules with 20 wt% $Na_2SO_4 \cdot 10H_2O$

Corresponding differential scanning calorimetry (DSC) trace

The hybrid structure showed high efficiency for **energy storage** applications with **thermal** and **chemical stability** after several cycles of thermal treatment. Although the **supercooling** problem still presents.

TEM micrograph of PU–Fe_3O_4 capsules with $Na_2(SO_4)_2 \cdot 10H_2O$ + $Na_2HPO_4 \cdot 2H_2O$ (20/0.4 wt%)

Corresponding differential scanning calorimetry (DSC) trace

A **nucleating agent ($Na_2HPO4 \cdot 2H_2O$)** was used to promote the crystallization of the PCM to **overcome the supercooling**.

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Hybrid Conducting Nanoparticles

Hybrid nanoparticles of polyaniline (PANI) or **polypyrrole (PPY)** are synthetized by **miniemulsion oxidative polymerization**.

Conductive properties are obtained as a result of the incorporation of CeO_2 nanoparticles. Those may be functionalized to increase the and the hydrophobicity of the cerium oxide(IV) using 3–(methacryloyloxy)propyl trimethoxysilane (MPS) as a functionalizing agent.

Once synthesized, the nanoparticles are used to produce films, which is a way to increase the applicability of the hybrid system.

Magnetic Catalytic Nanoparticles

Magnetoresponsive catalytic nanoparticles comprised of polystyrene and metal oxides (CeO_2 and Fe_3O_4) are prepared by **Pickering stabilization** (i.e., the use of inorganic nanoparticles for the stabilization of emulsions). This strategy is an alternative to previous routes of our team based on the in-situ crystallization on the particle surface.

Hydration of 2-cyanopiridine to 2-picolinamide

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Acknowledgements

- Financial support from the Max Planck Society (Germany) by the funding of the Max Planck Partner Group on Colloidal Methods for Multifunctional Materials (CM3-Lab).
- **Dr. David Vie** is gratefully acknowledged for continuous technical support.

MULTIFUNCTIONAL HYBRID COLLOIDS: ORGANICS AND INORGANICS MEET AT THE NANOSCALE

Inés Adam-Cervera[1,*], Juan F. Ferrer-Crespo[1,*], Francisco Pérez-Pla[1], Ana Torres-Suay[1], Olaia Álvarez-Bermúdez[1,2], Katharina Landfester[2], Clara M. Gómez[1], Rafael Muñoz-Espí[1,*]

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Colloidal methods, very especially those involving liquid–liquid heterophase systems, are very versatile for the preparation of polymer/inorganic hybrid nanoparticles and nanocapsules. On one hand, colloidal particles (both polymeric and inorganic) can act as a support for crystallization processes on their surface [1]. On the other hand, the colloidal structures generated by micelles and surfactant-stabilized droplets serve as soft templates or nanoreactors for the controlled precipitation of inorganic materials [2]. In this poster, we will provide an overview of the versatility of miniemulsion sytems for the synthesis of hybrid nanomaterials. We present four topics under current investigation by our team. In all four cases, the confinement of chemical processes at the nanoscale of systems stays in the foreground.

I. Design of chiral functionalities at the surface of polymer nanoparticles for metal complexation and asymmetric catalysis.

II. Thermal energy storage by encapsulation of phase change materials (PCMs) in either polyurethane/inorganic or poly(methyl methacrylate) nanocapsules.

III. Conducting hybrid nanoparticles of polyaniline or polypyrrole, incorporating CeO2 or Fe3O4 nanoparticles, applied in the formation of films.

IV. Magnetoresponsive catalytic nanoparticles comprised of polystyrene and metal oxides (CeO2 and Fe3O4), applied in the catalytic hydration of amides. Pickering stabilization is used for the nanoparticle synthesis [3].

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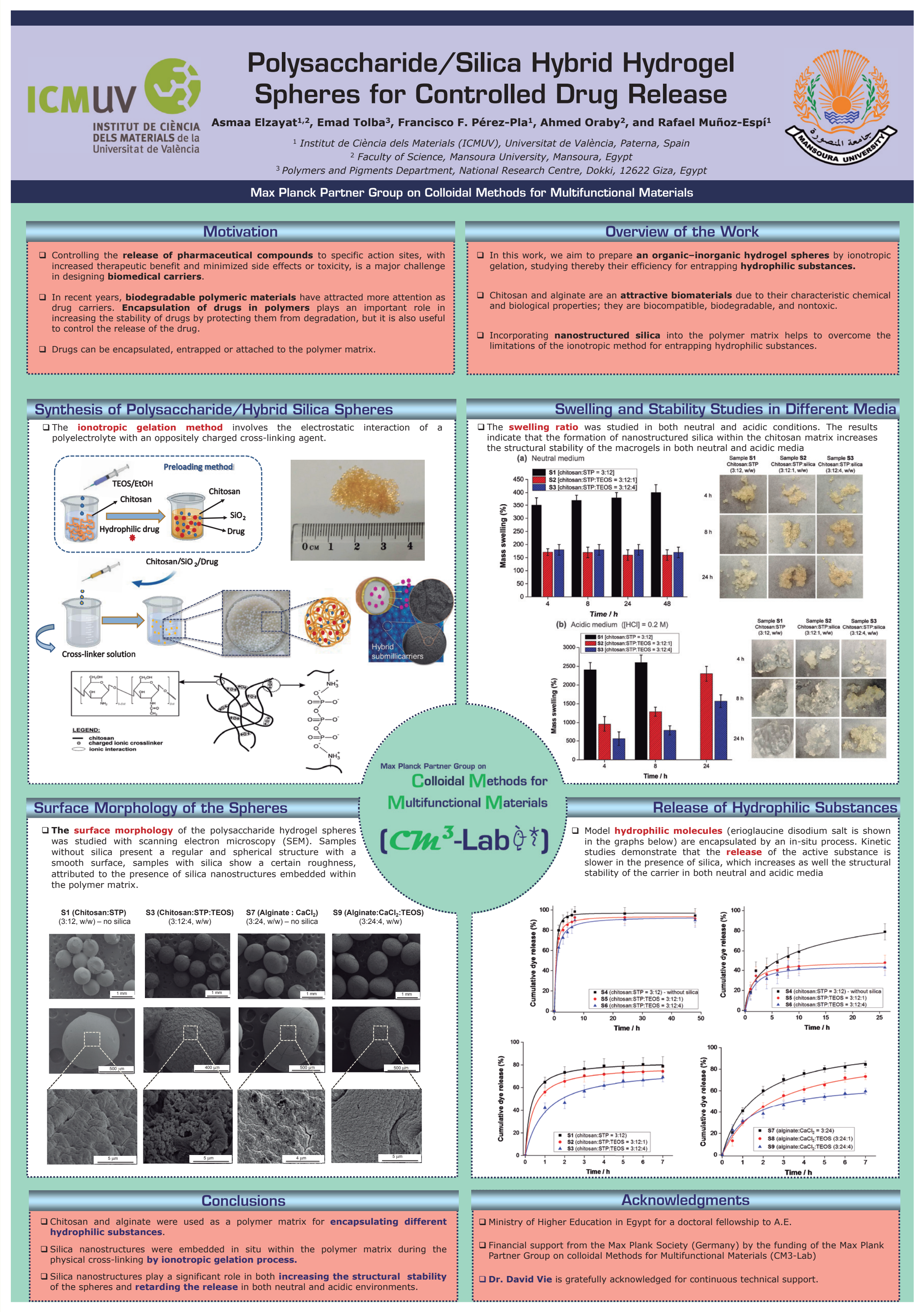

Polysaccharide/Silica Hybrid Hydrogel Spheres for Controlled Drug Release

Asmaa Elzayat[1,2], **Emad Tolba**[3], **Francisco F. Pérez-Pla**[1], **Ahmed Oraby**[2], and **Rafael Muñoz-Espí**[1]

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Max Planck Partner Group on Colloidal Methods for Multifunctional Materials

Motivation

- ❑ Controlling the **release of pharmaceutical compounds** to specific action sites, with increased therapeutic benefit and minimized side effects or toxicity, is a major challenge in designing **biomedical carriers**.
- ❑ In recent years, **biodegradable polymeric materials** have attracted more attention as drug carriers. **Encapsulation of drugs in polymers** plays an important role in increasing the stability of drugs by protecting them from degradation, but it is also useful to control the release of the drug.
- ❑ Drugs can be encapsulated, entrapped or attached to the polymer matrix.

Overview of the Work

- ❑ In this work, we aim to prepare **an organic–inorganic hydrogel spheres** by ionotropic gelation, studying thereby their efficiency for entrapping **hydrophilic substances.**
- ❑ Chitosan and alginate are an **attractive biomaterials** due to their characteristic chemical and biological properties; they are biocompatible, biodegradable, and nontoxic.
- ❑ Incorporating **nanostructured silica** into the polymer matrix helps to overcome the limitations of the ionotropic method for entrapping hydrophilic substances.

Synthesis of Polysaccharide/Hybrid Silica Spheres

- ❑ The **ionotropic gelation method** involves the electrostatic interaction of a polyelectrolyte with an oppositely charged cross-linking agent.

Swelling and Stability Studies in Different Media

- ❑ The **swelling ratio** was studied in both neutral and acidic conditions. The results indicate that the formation of nanostructured silica within the chitosan matrix increases the structural stability of the macrogels in both neutral and acidic media

Surface Morphology of the Spheres

- ❑ **The surface morphology** of the polysaccharide hydrogel spheres was studied with scanning electron microscopy (SEM). Samples without silica present a regular and spherical structure with a smooth surface, samples with silica show a certain roughness, attributed to the presence of silica nanostructures embedded within the polymer matrix.

Release of Hydrophilic Substances

- ❑ Model **hydrophilic molecules** (erioglaucine disodium salt is shown in the graphs below) are encapsulated by an in-situ process. Kinetic studies demonstrate that the **release** of the active substance is slower in the presence of silica, which increases as well the structural stability of the carrier in both neutral and acidic media

Conclusions

- ❑ Chitosan and alginate were used as a polymer matrix for **encapsulating different hydrophilic substances**.
- ❑ Silica nanostructures were embedded in situ within the polymer matrix during the physical cross-linking **by ionotropic gelation process.**
- ❑ Silica nanostructures play a significant role in both **increasing the structural stability** of the spheres and **retarding the release** in both neutral and acidic environments.

Acknowledgments

- ❑ Ministry of Higher Education in Egypt for a doctoral fellowship to A.E.
- ❑ Financial support from the Max Plank Society (Germany) by the funding of the Max Plank Partner Group on colloidal Methods for Multifunctional Materials (CM3-Lab)
- ❑ **Dr. David Vie** is gratefully acknowledged for continuous technical support.

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POLYSACCHARIDE/SILICA HYBRID HYDROGEL SPHERES FOR CONTROLLED DRUG RELEASE

Asmaa Elzayat[1,2,*], Emad Tolba[3], Francisco F. Pérez-Pla[1], Ahmed Oraby*, Rafael Muñoz-Espí[1,*]

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Controlling the release of pharmaceutical compounds to specific action sites, with increased therapeutic benefit and minimized side effects or toxicity, is a major challenge in designing biomedical micro- and nanocarriers. Encapsulation of drugs in polymers increases their stability by avoiding degradation, but it is also useful for controlling the release. In recent years, because of their biocompatibility and low or negligible toxicity, biodegradable polymer materials have attracted more attention as drug carriers.

In this work, organic–inorganic hydrogel spheres in the submillimeter scale were synthesized by ionotropic gelation and its efficiency for entrapping hydrophilic molecules was investigated. Chitosan or sodium alginate were used as a main component, and silica was used as a structuring additive. Different formulations were chosen to study how active hydrophilic molecules (erioglaucine disodium salt and ephedrine hydrochloride) can be entrapped inside the polymer matrix and how the subsequent release can be controlled by tailoring the network structure of the sol–gel matrix, in addition to improve the stability of the drug against enzymatic degradation of the gastrointestinal tract. Besides the increase of stability as a result of the silica incorporation (compare panels a and b in Figure 1), kinetic studies demonstrated that the release of the active substance is slower in the presence of silica in both neutral and acid medium.

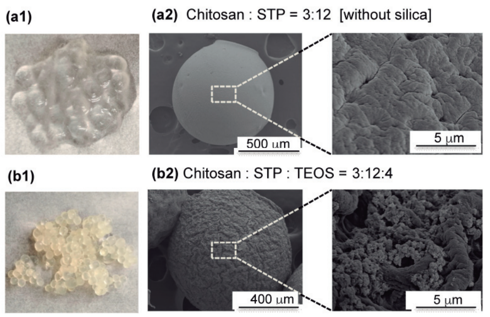
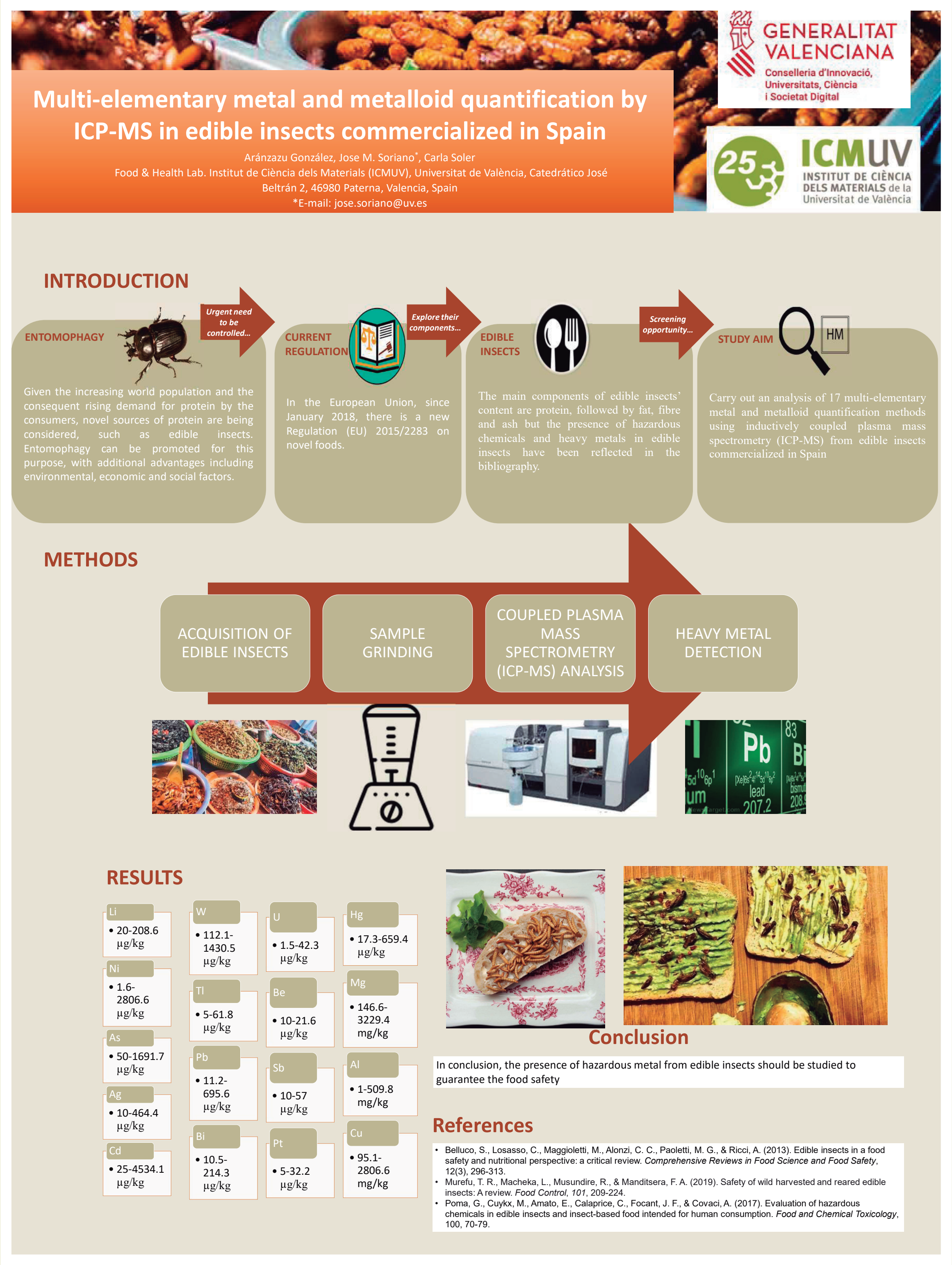


Figure 1. (a) Chitosan particles and (b) chitosan–silica hybrid particles prepared by ionotropic gelation: (1) photograph after 24 h in highly acidic conditions ([HCl] = 0.2 M); (2) SEM images of a particle as prepared.



Multi-elementary metal and metalloid quantification by ICP-MS in edible insects commercialized in Spain

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INTRODUCTION

ENTOMOPHAGY

Given the increasing world population and the consequent rising demand for protein by the consumers, novel sources of protein are being considered, such as edible insects. Entomophagy can be promoted for this purpose, with additional advantages including environmental, economic and social factors.

Urgent need to be controlled…

CURRENT REGULATION

In the European Union, since January 2018, there is a new Regulation (EU) 2015/2283 on novel foods.

Explore their components…

EDIBLE INSECTS

The main components of edible insects' content are protein, followed by fat, fibre and ash but the presence of hazardous chemicals and heavy metals in edible insects have been reflected in the bibliography.

Screening opportunity…

STUDY AIM

Carry out an analysis of 17 multi-elementary metal and metalloid quantification methods using inductively coupled plasma mass spectrometry (ICP-MS) from edible insects commercialized in Spain

METHODS

ACQUISITION OF EDIBLE INSECTS
SAMPLE GRINDING
COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) ANALYSIS
HEAVY METAL DETECTION

RESULTS

Li	20-208.6 µg/kg
Ni	1.6-2806.6 µg/kg
As	50-1691.7 µg/kg
Ag	10-464.4 µg/kg
Cd	25-4534.1 µg/kg
W	112.1-1430.5 µg/kg
Tl	5-61.8 µg/kg
Pb	11.2-695.6 µg/kg
Bi	10.5-214.3 µg/kg
U	1.5-42.3 µg/kg
Be	10-21.6 µg/kg
Sb	10-57 µg/kg
Pt	5-32.2 µg/kg
Hg	17.3-659.4 µg/kg
Mg	146.6-3229.4 mg/kg
Al	1-509.8 mg/kg
Cu	95.1-2806.6 mg/kg

Conclusion

In conclusion, the presence of hazardous metal from edible insects should be studied to guarantee the food safety

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METAL AND METALLOID MULTI-ELEMENTARY ICP-MS IN EDIBLE INSECTS COMMERCIALIZED IN SPAIN

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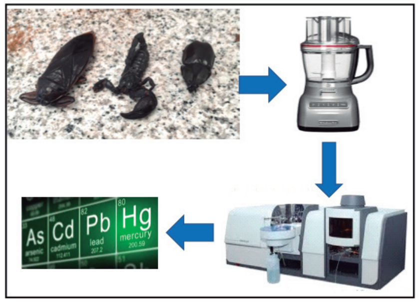
Entomophagy is an alternative protein source for human food and animal feed, with additional advantages including environmental, economic and social factors [1]. In the European Union, since January 2018, there is a new Regulation (EU) 2015/2283 on novel foods. This regulation lays down rules for the placing of novel foods on the market within the Union. Its purpose is to ensure the effective functioning of the internal market while providing a high level of protection of human health and consumers' interests. The main components of edible insects' content are protein, followed by fat, fibre and ash but the presence of hazardous chemicals and heavy metals in edible insects have been reflected in the bibliography [2]. The aim of this study is carried out an analysis of seventeen multi-elementary metal and metalloid quantification methods using inductively coupled plasma mass spectrometry (ICP-MS) from edible insects (Figure 1) commercialized in Spain. Range of values were <20-208.6, 1,6-2806.6, <50-1691.7, <10-464.4, <25-4534.1, 112.1-1430.5, <5-61.8, 11.2-695.6, 10.5-214.3, <1.5-42.3, <10-21.6, <10-57, <5-32.2 and 17.3-659.4 µg/kg, 146.6-3229.4, <1-509.8, 95.1-2806.6 mg/kg from Li, Ni, As, Ag, Cd, W, Tl, Pb, Bi, U, Be, Sb, Pt, Hg, Mg, Al and Cu, respectively.



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What does Paella Valenciana contain? Ingredients and materials used in cooking procedures during 20th and 21st centuries

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Introduction

Paella Valenciana is a Spanish dish originally from Valencia, which is cooked with an ingredient list protected by a Designation of Origin, as are round rice (from Valencia, in Bomba or Albufera, but absolutely round and short rice) and olive oil (from Valencia, or any Mediterranean extra virgin oil) since the end of 2011. It is usually cooked with firewood but it is possible to cook it with gas. The paella Valenciana has quite a history but etymological problems have affected the concept not only of the material used for its cooking but also in terms of its ingredients in the last decades.

Objective

The aim of this study is to review paella Valencia concept from historic and culinary perspectives during 20th and 21st centuries.

Results

Results reflected that the paella term is used incorrectly in 5, 7, 75 and 79% from the literature, grey literature, social media and webpages, respectively. In fact, in some of this bibliographic sources the paella valenciana is defined as "a dish that is made with those ingredients that you have available and throwing everything in the paella". On contrary, in other manuscripts the elaboration of the recipe appears meticulously detailed.

The ingredients found throughout history are different, such as chicken, duck, pork, chorizo in meat and artichoke, peas, green beans or peppers for vegetables. However, the standard ingredients of paella valenciana are rice, chicken, rabbit, saffron, grated fresh tomato, ferraura, rotjet or wide green bean, garrofo beans, water, virgin olive oil and salt being results obtained in the bibliographic review are wrong in the 48% of cookbooks from both centuries.

Conclusions

The concept paella has always generated confusion. Paella Valenciana nomenclature has been defined in the first half of the XXI century.

In order to protect the recipe and differentiate it from other rice dishes cooked in paella, la paella valenciana includes ten standard ingredients and other supported variants and employs very precise culinary technique.

The rest of the rice dishes would be called "paellas de" to recipes cooked in paella, or "arroz con", when using other containers.

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WHAT DOES PAELLA VALENCIANA CONTAIN?

INGREDIENTS AND MATERIALS USED IN COOKING PROCEDURES DURING 20TH AND 21ST CENTURIES

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Paella Valenciana is a Spanish dish originally from Valencia, which is cooked with an ingredient list protected by a Designation of Origin, as are round rice (from Valencia, in Bomba or Albufera, but absolutely round and short rice) and olive oil (from Valencia, or any Mediterranean extra virgin oil) since the end of 2011. It is usually cooked with firewood but it is possible to cook it with gas. The paella Valenciana has quite a history but etymological problems have affected the concept not only of the material used for its cooking but also in terms of its ingredients in the last decades. The aim of this study is to review paella Valencia concept from historic and culinary perspectives during 20th and 21st centuries. Results reflected that the paella term is used incorrectly in 5, 7, 75 and 79% from the literature, grey literature, social media and webpages, respectively. Furthermore, the standard ingredients [3] of paella valenciana are rice, chicken, rabbit, saffron, grated fresh tomato, ferraura, rotjet or wide green bean, garrofo beans, water, virgin olive oil and salt (Figure 1) being results obtained in the bibliographic review are wrong in the 48% of cookbooks from both centuries.

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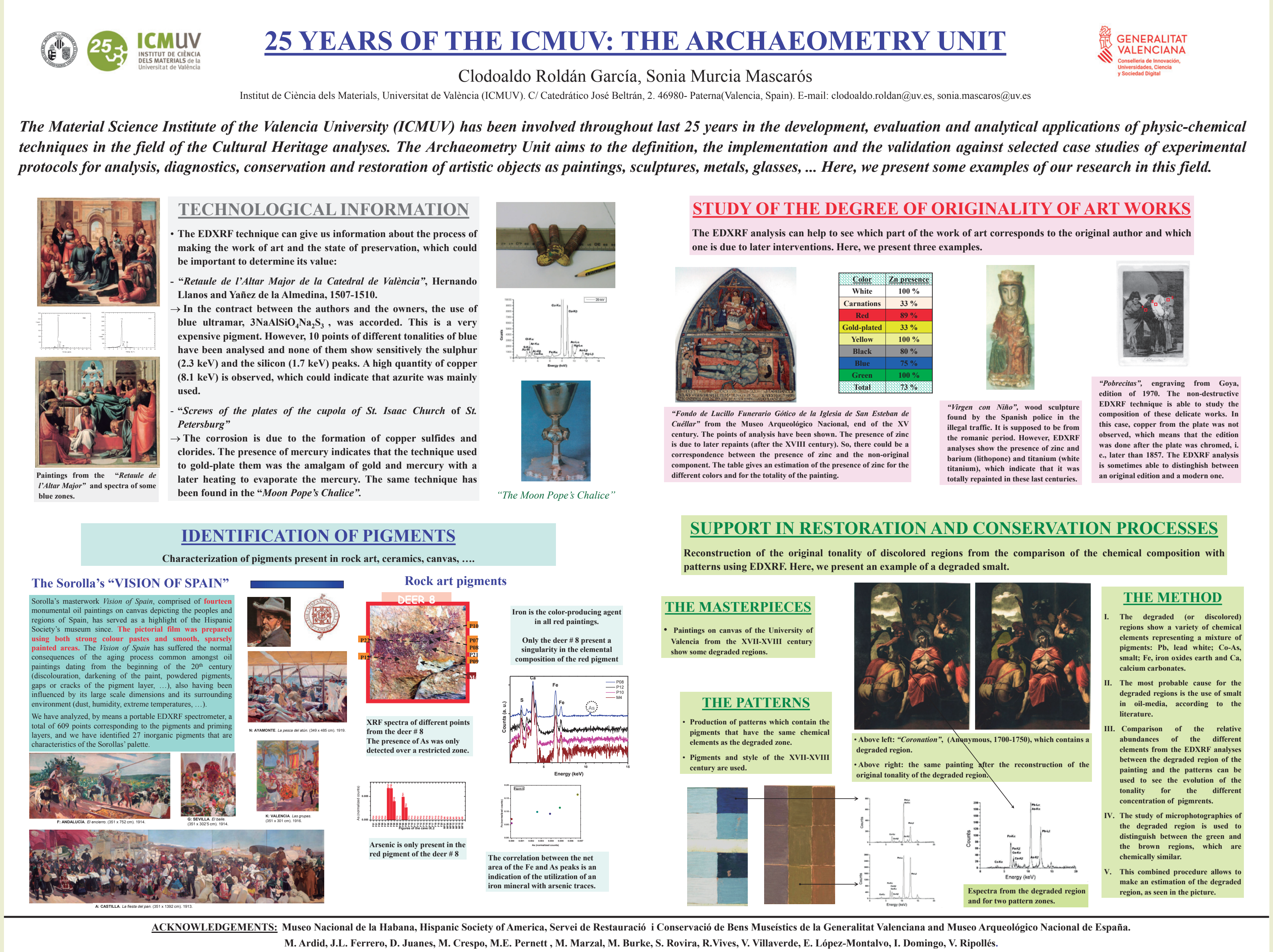

25 YEARS OF THE ICMUV: THE ARCHAEOMETRY UNIT

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The Material Science Institute of the Valencia University (ICMUV) has been involved throughout last 25 years in the development, evaluation and analytical applications of physic-chemical techniques in the field of the Cultural Heritage analyses. The Archaeometry Unit aims to the definition, the implementation and the validation against selected case studies of experimental protocols for analysis, diagnostics, conservation and restoration of artistic objects as paintings, sculptures, metals, glasses, ... Here, we present some examples of our research in this field.

TECHNOLOGICAL INFORMATION

- The EDXRF technique can give us information about the process of making the work of art and the state of preservation, which could be important to determine its value:

- "*Retaule de l'Altar Major de la Catedral de València*", Hernando Llanos and Yañez de la Almedina, 1507-1510.

→ In the contract between the authors and the owners, the use of blue ultramar, $3NaAlSiO_4Na_2S_3$, was accorded. This is a very expensive pigment. However, 10 points of different tonalities of blue have been analysed and none of them show sensitively the sulphur (2.3 keV) and the silicon (1.7 keV) peaks. A high quantity of copper (8.1 keV) is observed, which could indicate that azurite was mainly used.

- "*Screws of the plates of the cupola of St. Isaac Church* of *St. Petersburg*"

→ The corrosion is due to the formation of copper sulfides and clorides. The presence of mercury indicates that the technique used to gold-plate them was the amalgam of gold and mercury with a later heating to evaporate the mercury. The same technique has been found in the "*Moon Pope's Chalice*".

Paintings from the "*Retaule de l'Altar Major*" and spectra of some blue zones.

"The Moon Pope's Chalice"

STUDY OF THE DEGREE OF ORIGINALITY OF ART WORKS

The EDXRF analysis can help to see which part of the work of art corresponds to the original author and which one is due to later interventions. Here, we present three examples.

Color	Zn presence
White	100 %
Carnations	33 %
Red	89 %
Gold-plated	33 %
Yellow	100 %
Black	80 %
Blue	75 %
Green	100 %
Total	73 %

"*Fondo de Lucillo Funerario Gótico de la Iglesia de San Esteban de Cuéllar*" from the Museo Arqueológico Nacional, end of the XV century. The points of analysis have been shown. The presence of zinc is due to later repaints (after the XVIII century). So, there could be a correspondence between the presence of zinc and the non-original component. The table gives an estimation of the presence of zinc for the different colors and for the totality of the painting.

"*Virgen con Niño*", wood sculpture found by the Spanish police in the illegal traffic. It is supposed to be from the romanic period. However, EDXRF analyses show the presence of zinc and barium (lithopone) and titanium (white titanium), which indicate that it was totally repainted in these last centuries.

"*Pobrecitas*", engraving from Goya, edition of 1970. The non-destructive EDXRF technique is able to study the composition of these delicate works. In this case, copper from the plate was not observed, which means that the edition was done after the plate was chromed, i. e., later than 1857. The EDXRF analysis is sometimes able to distinghish between an original edition and a modern one.

IDENTIFICATION OF PIGMENTS

Characterization of pigments present in rock art, ceramics, canvas, ….

The Sorolla's "VISION OF SPAIN"

Sorolla's masterwork *Vision of Spain*, comprised of **fourteen** monumental oil paintings on canvas depicting the peoples and regions of Spain, has served as a highlight of the Hispanic Society's museum since. **The pictorial film was prepared using both strong colour pastes and smooth, sparsely painted areas.** The *Vision of Spain* has suffered the normal consequences of the aging process common amongst oil paintings dating from the beginning of the 20th century (discolouration, darkening of the paint, powdered pigments, gaps or cracks of the pigment layer, …), also having been influenced by its large scale dimensions and its surrounding environment (dust, humidity, extreme temperatures, …).

We have analyzed, by means a portable EDXRF spectrometer, a total of 609 points corresponding to the pigments and priming layers, and we have identified 27 inorganic pigments that are characteristics of the Sorollas' palette.

N: AYAMONTE. *La pesca del atún*. (349 x 485 cm). 1919.

F: ANDALUCÍA. *El encierro*. (351 x 752 cm). 1914.

G: SEVILLA. *El baile*. (351 x 302'5 cm). 1914.

K: VALENCIA. *Las grupas*. (351 x 301 cm). 1916.

A: CASTILLA. *La fiesta del pan*. (351 x 1392 cm). 1913.

Rock art pigments

Iron is the color-producing agent in all red paintings.

Only the deer # 8 present a singularity in the elemental composition of the red pigment

XRF spectra of different points from the deer # 8
The presence of As was only detected over a restricted zone.

Arsenic is only present in the red pigment of the deer # 8

The correlation between the net area of the Fe and As peaks is an indication of the utilization of an iron mineral with arsenic traces.

SUPPORT IN RESTORATION AND CONSERVATION PROCESSES

Reconstruction of the original tonality of discolored regions from the comparison of the chemical composition with patterns using EDXRF. Here, we present an example of a degraded smalt.

THE MASTERPIECES

- Paintings on canvas of the University of Valencia from the XVII-XVIII century show some degraded regions.

THE PATTERNS

- Production of patterns which contain the pigments that have the same chemical elements as the degraded zone.
- Pigments and style of the XVII-XVIII century are used.

- Above left: "*Coronation*", (Anonymous, 1700-1750), which contains a degraded region.
- Above right: the same painting after the reconstruction of the original tonality of the degraded region.

Espectra from the degraded region and for two pattern zones.

THE METHOD

I. The degraded (or discolored) regions show a variety of chemical elements representing a mixture of pigments: Pb, lead white; Co-As, smalt; Fe, iron oxides earth and Ca, calcium carbonates.
II. The most probable cause for the degraded regions is the use of smalt in oil-media, according to the literature.
III. Comparison of the relative abundances of the different elements from the EDXRF analyses between the degraded region of the painting and the patterns can be used to see the evolution of the tonality for the different concentration of pigmrents.
IV. The study of microphotographies of the degraded region is used to distinguish between the green and the brown regions, which are chemically similar.
V. This combined procedure allows to make an estimation of the degraded region, as seen in the picture.

ACKNOWLEDGEMENTS: Museo Nacional de la Habana, Hispanic Society of America, Servei de Restauració i Conservació de Bens Museístics de la Generalitat Valenciana and Museo Arqueológico Nacional de España.
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25 YEARS OF THE ICMUV: THE ARCHAEOMETRY UNIT

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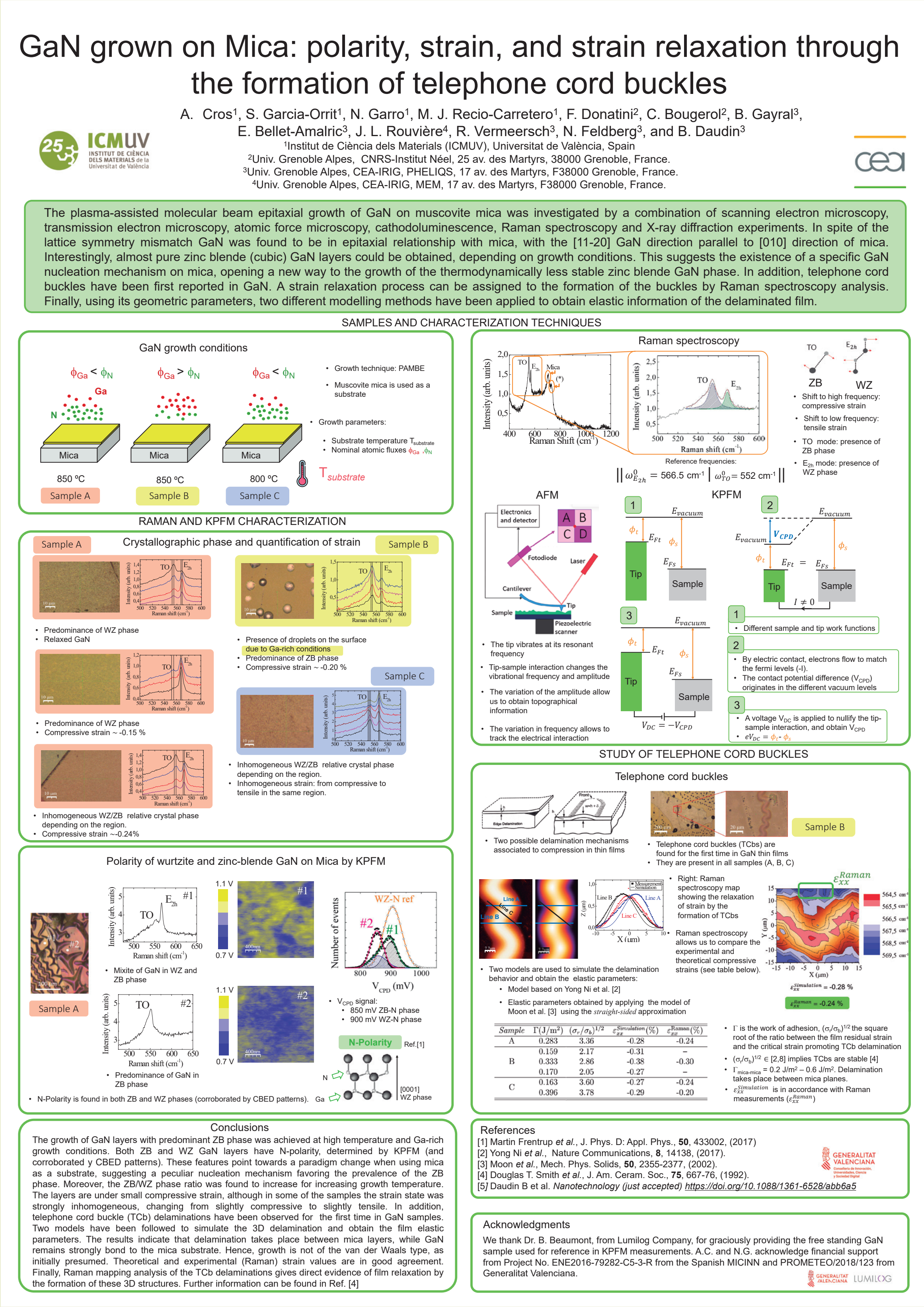
The Material Science Institute of the Valencia University (ICMUV) has been involved throughout the last 25 years in the development, evaluation and analytical applications of physic-chemical techniques in the field of the Cultural Heritage analyses. The Archaeometry Unit aims to the definition, the implementation and the validation against selected case studies of experimental protocols for analysis, diagnostics, conservation and restoration of artistic objects as paintings, sculptures, metals, glasses, ... Here, we present some examples that give an idea of our research.



GaN grown on Mica: polarity, strain, and strain relaxation through the formation of telephone cord buckles

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The plasma-assisted molecular beam epitaxial growth of GaN on muscovite mica was investigated by a combination of scanning electron microscopy, transmission electron microscopy, atomic force microscopy, cathodoluminescence, Raman spectroscopy and X-ray diffraction experiments. In spite of the lattice symmetry mismatch GaN was found to be in epitaxial relationship with mica, with the [11-20] GaN direction parallel to [010] direction of mica. Interestingly, almost pure zinc blende (cubic) GaN layers could be obtained, depending on growth conditions. This suggests the existence of a specific GaN nucleation mechanism on mica, opening a new way to the growth of the thermodynamically less stable zinc blende GaN phase. In addition, telephone cord buckles have been first reported in GaN. A strain relaxation process can be assigned to the formation of the buckles by Raman spectroscopy analysis. Finally, using its geometric parameters, two different modelling methods have been applied to obtain elastic information of the delaminated film.

SAMPLES AND CHARACTERIZATION TECHNIQUES

GaN growth conditions

- Growth technique: PAMBE
- Muscovite mica is used as a substrate
- Growth parameters:
  - Substrate temperature $T_{substrate}$
  - Nominal atomic fluxes ϕ_{Ga} ,ϕ_N

Raman spectroscopy

Reference frequencies:

$$\omega^0_{E_{2h}} = 566.5 \text{ cm}^{-1} \quad \omega^0_{TO} = 552 \text{ cm}^{-1}$$

- Shift to high frequency: compressive strain
- Shift to low frequency: tensile strain
- TO mode: presence of ZB phase
- E_{2h} mode: presence of WZ phase

AFM

- The tip vibrates at its resonant frequency
- Tip-sample interaction changes the vibrational frequency and amplitude
- The variation of the amplitude allow us to obtain topographical information
- The variation in frequency allows to track the electrical interaction

KPFM

1
- Different sample and tip work functions

2
- By electric contact, electrons flow to match the fermi levels (-I).
- The contact potential difference (V_{CPD}) originates in the different vacuum levels

3
- A voltage V_{DC} is applied to nullify the tip-sample interaction, and obtain V_{CPD}
- $eV_{DC} = \phi_t - \phi_s$

RAMAN AND KPFM CHARACTERIZATION

Crystallographic phase and quantification of strain

Sample A

- Predominance of WZ phase
- Relaxed GaN

- Predominance of WZ phase
- Compressive strain ~ -0.15 %

- Inhomogeneous WZ/ZB relative crystal phase depending on the region.
- Compressive strain ~-0.24%

Sample B

- Presence of droplets on the surface due to Ga-rich conditions
- Predominance of ZB phase
- Compressive strain ~ -0.20 %

Sample C

- Inhomogeneous WZ/ZB relative crystal phase depending on the region.
- Inhomogeneous strain: from compressive to tensile in the same region.

Polarity of wurtzite and zinc-blende GaN on Mica by KPFM

Sample A

- Mixite of GaN in WZ and ZB phase
- Predominance of GaN in ZB phase
- V_{CPD} signal:
  - 850 mV ZB-N phase
  - 900 mV WZ-N phase

N-Polarity Ref.[1]

- N-Polarity is found in both ZB and WZ phases (corroborated by CBED patterns).

STUDY OF TELEPHONE CORD BUCKLES

Telephone cord buckles

- Two possible delamination mechanisms associated to compression in thin films

Sample B

- Telephone cord buckles (TCbs) are found for the first time in GaN thin films
- They are present in all samples (A, B, C)

- Right: Raman spectroscopy map showing the relaxation of strain by the formation of TCbs
- Raman spectroscopy allows us to compare the experimental and theoretical compressive strains (see table below).

$\varepsilon_{xx}^{Simulation}$ = -0.28 %

ε_{xx}^{Raman} = -0.24 %

- Two models are used to simulate the delamination behavior and obtain the elastic parameters:
  - Model based on Yong Ni et al. [2]
  - Elastic parameters obtained by applying the model of Moon et al. [3] using the *straight-sided* approximation

Sample	$\Gamma(\text{J/m}^2)$	$(\sigma_r/\sigma_b)^{1/2}$	$\varepsilon_{xx}^{Simulation}(\%)$	$\varepsilon_{xx}^{Raman}(\%)$
A	0.283	3.36	-0.28	-0.24
B	0.159	2.17	-0.31	–
	0.333	2.86	-0.38	-0.30
	0.170	2.05	-0.27	–
C	0.163	3.60	-0.27	-0.24
	0.396	3.78	-0.29	-0.20

- Γ is the work of adhesion, $(\sigma_r/\sigma_b)^{1/2}$ the square root of the ratio between the film residual strain and the critical strain promoting TCb delamination
- $(\sigma_r/\sigma_b)^{1/2} \in [2,8]$ implies TCbs are stable [4]
- $\Gamma_{mica\text{-}mica}$ = 0.2 J/m² – 0.6 J/m². Delamination takes place between mica planes.
- $\varepsilon_{xx}^{Simulation}$ is in accordance with Raman measurements (ε_{xx}^{Raman})

Conclusions

The growth of GaN layers with predominant ZB phase was achieved at high temperature and Ga-rich growth conditions. Both ZB and WZ GaN layers have N-polarity, determined by KPFM (and corroborated y CBED patterns). These features point towards a paradigm change when using mica as a substrate, suggesting a peculiar nucleation mechanism favoring the prevalence of the ZB phase. Moreover, the ZB/WZ phase ratio was found to increase for increasing growth temperature. The layers are under small compressive strain, although in some of the samples the strain state was strongly inhomogeneous, changing from slightly compressive to slightly tensile. In addition, telephone cord buckle (TCb) delaminations have been observed for the first time in GaN samples. Two models have been followed to simulate the 3D delamination and obtain the film elastic parameters. The results indicate that delamination takes place between mica layers, while GaN remains strongly bond to the mica substrate. Hence, growth is not of the van der Waals type, as initially presumed. Theoretical and experimental (Raman) strain values are in good agreement. Finally, Raman mapping analysis of the TCb delaminations gives direct evidence of film relaxation by the formation of these 3D structures. Further information can be found in Ref. [4]

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GaN GROWN ON MICA: POLARITY, STRAIN, AND STRAIN RELAXATION THROUGH THE FORMATION OF TELEPHONE CORD BUCKLES

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The use of exotic substrates such as lamellar ones is a current strategy to circumvent the lattice parameter mismatch issue faced when growing semiconductor materials on more conventional substrates. Here we study crystal structure, morphology and strain relaxation of GaN layers grown by molecular beam epitaxy (MBE) on muscovite mica, a transparent layered material that becomes flexible if it is sufficiently thin (tens of microns). The continuous layers obtained grow along [000-1] (N-polarity). As in pulsed laser deposition growth [1], the wurtzite [11-20] direction is aligned to the [010] direction of mica. Remarkably, depending on MBE growth conditions, almost pure zinc-blende material can be obtained. The cubic phase grows along [111] and is also N-terminated. Most interestingly, in spite of the crystallographic lattice mismatch between GaN and Mica [2], the 250 nm thick layers grow with a small compressive strain (~0.18%) that varies slightly with location. This partial relaxation is ascribed to the easy delamination of mica just below the GaN/substrate interface, while a thin layer of mica remains chemically bond to GaN. Further relaxation of GaN takes place by the formation of three-dimensional structures in the shape of telephone cord buckles, straight blisters or by more complex arrangements]. In this work we use Raman scattering and atomic force microscopy (AFM) maps to study the characteristics of GaN telephone cord buckles (width, height, period and symmetry) in relation to the compressive strain of the surrounding material, the achieved relaxation and layer adhesion. These parameters will be analyzed in comparison with the elastic model recently developed by Ni et al. [3] and the adhesion measurements proposed by Cordill et al. [4]. To the best of our knowledge, this is the first report of the formation of telephone cord buckles in GaN.

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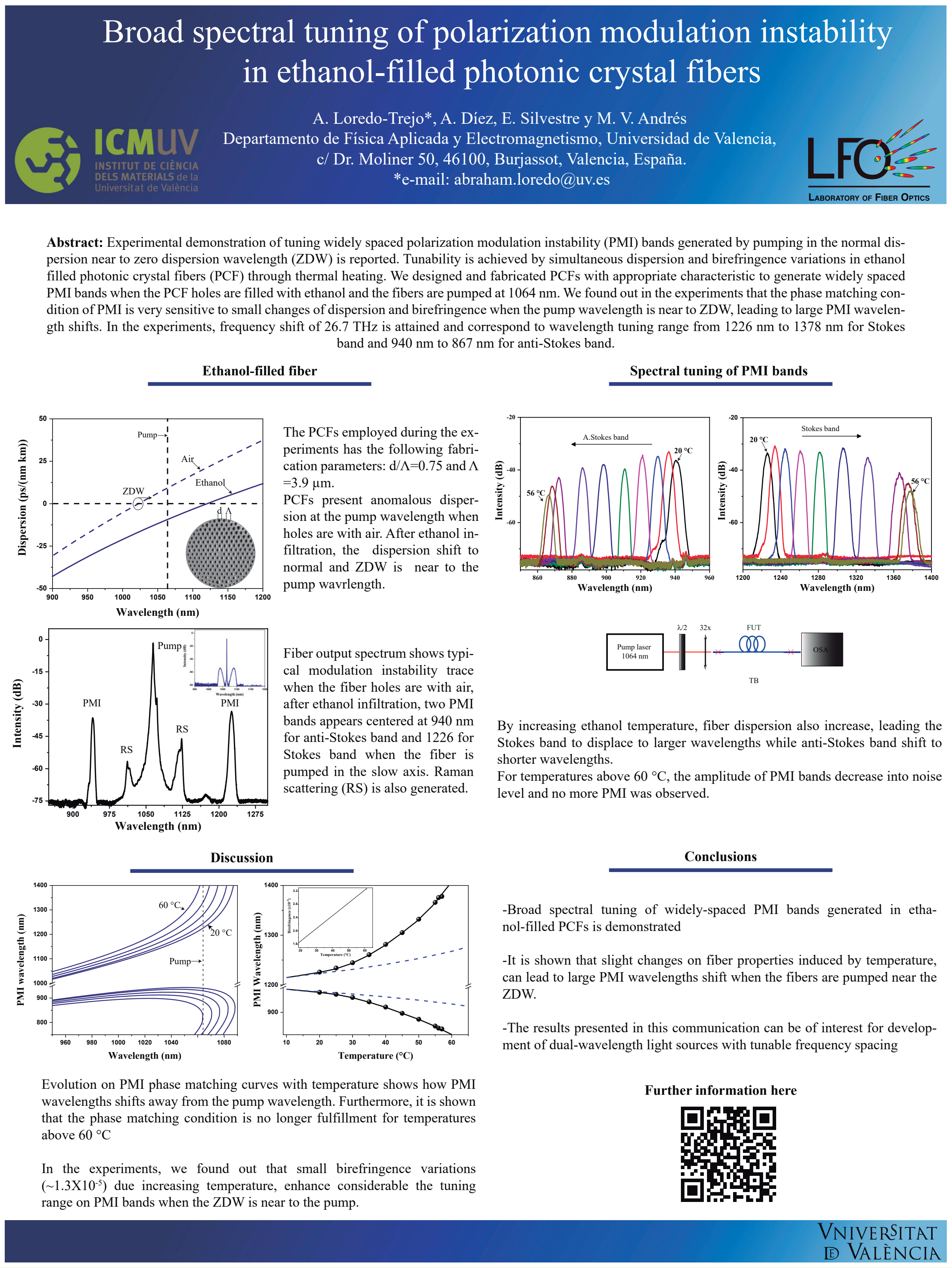

Broad spectral tuning of polarization modulation instability in ethanol-filled photonic crystal fibers

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Abstract: Experimental demonstration of tuning widely spaced polarization modulation instability (PMI) bands generated by pumping in the normal dispersion near to zero dispersion wavelength (ZDW) is reported. Tunability is achieved by simultaneous dispersion and birefringence variations in ethanol filled photonic crystal fibers (PCF) through thermal heating. We designed and fabricated PCFs with appropriate characteristic to generate widely spaced PMI bands when the PCF holes are filled with ethanol and the fibers are pumped at 1064 nm. We found out in the experiments that the phase matching condition of PMI is very sensitive to small changes of dispersion and birefringence when the pump wavelength is near to ZDW, leading to large PMI wavelength shifts. In the experiments, frequency shift of 26.7 THz is attained and correspond to wavelength tuning range from 1226 nm to 1378 nm for Stokes band and 940 nm to 867 nm for anti-Stokes band.

Ethanol-filled fiber

The PCFs employed during the experiments has the following fabrication parameters: d/Λ=0.75 and Λ =3.9 µm.

PCFs present anomalous dispersion at the pump wavelength when holes are with air. After ethanol infiltration, the dispersion shift to normal and ZDW is near to the pump wavrlength.

Fiber output spectrum shows typical modulation instability trace when the fiber holes are with air, after ethanol infiltration, two PMI bands appears centered at 940 nm for anti-Stokes band and 1226 for Stokes band when the fiber is pumped in the slow axis. Raman scattering (RS) is also generated.

Spectral tuning of PMI bands

By increasing ethanol temperature, fiber dispersion also increase, leading the Stokes band to displace to larger wavelengths while anti-Stokes band shift to shorter wavelengths.

For temperatures above 60 °C, the amplitude of PMI bands decrease into noise level and no more PMI was observed.

Discussion

Evolution on PMI phase matching curves with temperature shows how PMI wavelengths shifts away from the pump wavelength. Furthermore, it is shown that the phase matching condition is no longer fulfillment for temperatures above 60 °C

In the experiments, we found out that small birefringence variations (~1.3X10^{-5}) due increasing temperature, enhance considerable the tuning range on PMI bands when the ZDW is near to the pump.

Conclusions

-Broad spectral tuning of widely-spaced PMI bands generated in ethanol-filled PCFs is demonstrated

-It is shown that slight changes on fiber properties induced by temperature, can lead to large PMI wavelengths shift when the fibers are pumped near the ZDW.

-The results presented in this communication can be of interest for development of dual-wavelength light sources with tunable frequency spacing

Further information here

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BROAD SPECTRAL TUNING OF POLARIZATION MODULATION INSTABILITY IN ETHANOL-FILLED PHOTONIC CRYSTAL FIBERS

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Polarization modulation instability (PMI) is a nonlinear effect where two pump photons with identical polarization propagating in nonlinear medium give rise to two new photons of different frequency and orthogonal polarization respect to the initial photons [1]. In this work we present experimentally broad spectral tuning of PMI in ethanol-filled photonic crystal fibers (PCF) with normal dispersion pump at 1064 nm. Ethanol-filled PCFs were designed and fabricated with the appropriate characteristics to produce widely spaced PMI bands when the fiber is pumped at 1064 nm (see fig. 1(a)-(b)). Tuning effect is achieved by exploiting the strong PMI dependence to dispersion-birefringence variations. In the experiments, tunability is accomplished by changes in the infiltrated ethanol refractive index through thermal heating, i.e. changes in PCF refractive index profile modifies the chromatic dispersion and modal birefringence of the fiber, reflecting as a spectral shift in PMI bands when increasing temperature. Ethanol has been chosen due to its large thermo-optic coefficient (~3.9x10-4 K-1). Frequency tuning range from 1236 cm-1 to 2142 cm-1 in a temperature span of 20 °C to 56 °C is obtained in the experiments, as is shown in fig. 1 (c)-(d). These results can be of interest in development of dual-wavelength light sources based on PMI. Further information can be found in [2].

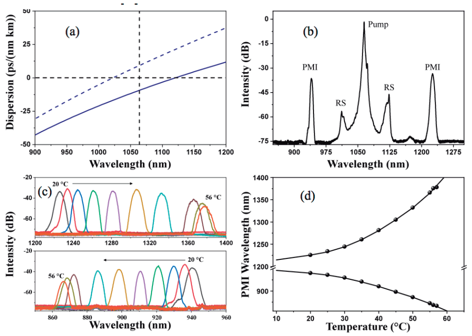

Fig. 1 (a) PCF chromatic dispersion as a function of wavelength, filled with air (solid) and with ethanol (dash), vertical dashed lines indicate experimental pump wavelength. (b) Light spectrum at the output of ethanol-filled PCF, (c) PMI bands for different temperatures from 20 °C to 56 °C. (d) PMI wavelengths as a function of temperature. Dots are experimental data and lines are theoretical calculations.

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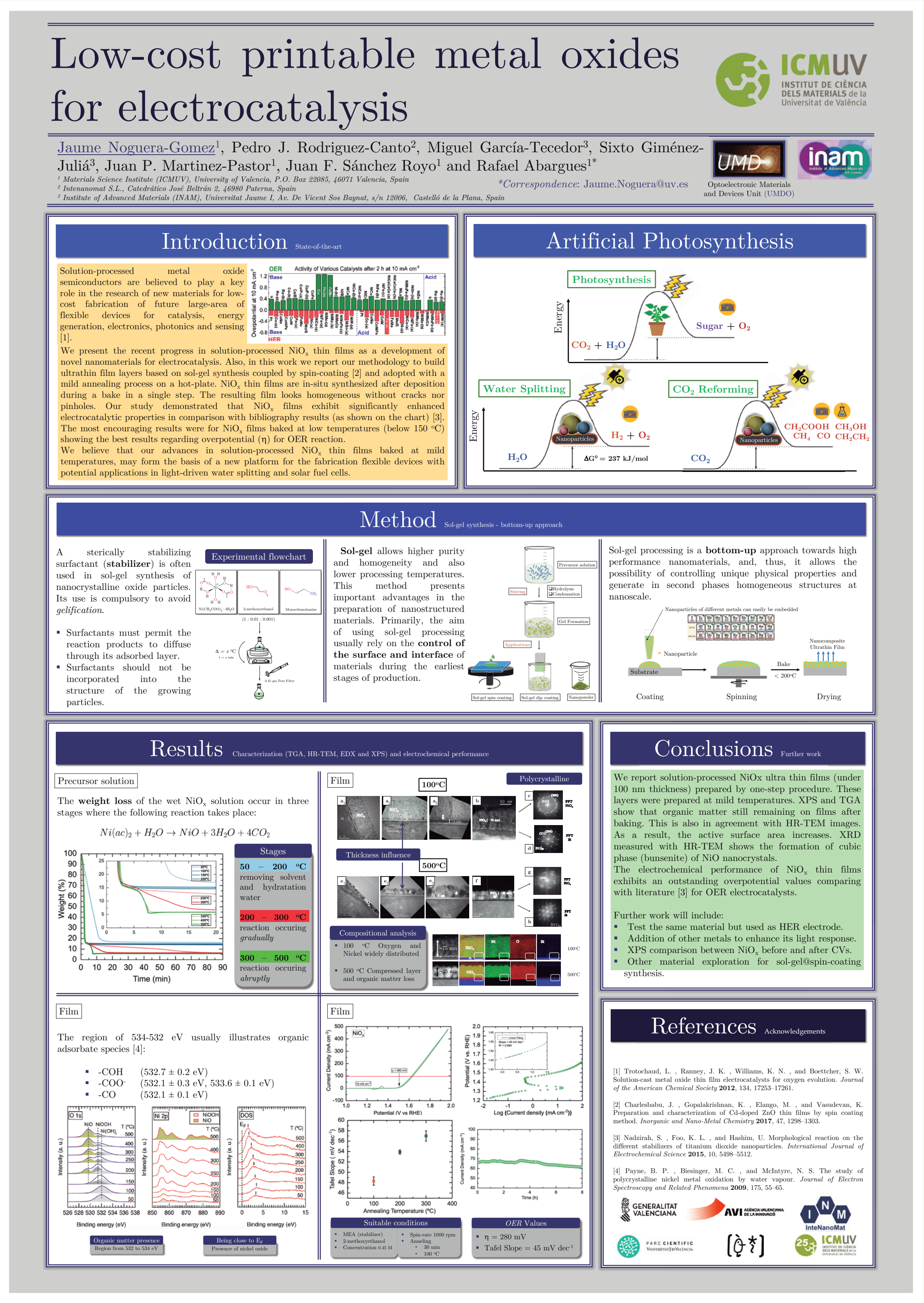

Low-cost printable metal oxides for electrocatalysis

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Optoelectronic Materials and Devices Unit (UMDO)

Introduction State-of-the-art

Solution-processed metal oxide semiconductors are believed to play a key role in the research of new materials for low-cost fabrication of future large-area of flexible devices for catalysis, energy generation, electronics, photonics and sensing [1].

We present the recent progress in solution-processed NiO_x thin films as a development of novel nanomaterials for electrocatalysis. Also, in this work we report our methodology to build ultrathin film layers based on sol-gel synthesis coupled by spin-coating [2] and adopted with a mild annealing process on a hot-plate. NiO_x thin films are in-situ synthesized after deposition during a bake in a single step. The resulting film looks homogeneous without cracks nor pinholes. Our study demonstrated that NiO_x films exhibit significantly enhanced electrocatalytic properties in comparison with bibliography results (as shown on the chart) [3]. The most encouraging results were for NiO_x films baked at low temperatures (below 150 ºC) showing the best results regarding overpotential (η) for OER reaction.

We believe that our advances in solution-processed NiO_x thin films baked at mild temperatures, may form the basis of a new platform for the fabrication flexible devices with potential applications in light-driven water splitting and solar fuel cells.

Artificial Photosynthesis

Method Sol-gel synthesis - bottom-up approach

A sterically stabilizing surfactant (**stabilizer**) is often used in sol-gel synthesis of nanocrystalline oxide particles. Its use is compulsory to avoid *gelification*.

- Surfactants must permit the reaction products to diffuse through its adsorbed layer.
- Surfactants should not be incorporated into the structure of the growing particles.

Experimental flowchart

Sol-gel allows higher purity and homogeneity and also lower processing temperatures. This method presents important advantages in the preparation of nanostructured materials. Primarily, the aim of using sol-gel processing usually rely on the **control of the surface and interface** of materials during the earliest stages of production.

Sol-gel processing is a **bottom-up** approach towards high performance nanomaterials, and, thus, it allows the possibility of controlling unique physical properties and generate in second phases homogeneous structures at nanoscale.

Results Characterization (TGA, HR-TEM, EDX and XPS) and electrochemical performance

Precursor solution

The **weight loss** of the wet NiO_x solution occur in three stages where the following reaction takes place:

$$Ni(ac)_2 + H_2O \rightarrow NiO + 3H_2O + 4CO_2$$

Stages

- 50 – 200 ºC removing solvent and hydratation water
- 200 – 300 ºC reaction occuring *gradually*
- 300 – 500 ºC reaction occuring *abruptly*

Film

Compositional analysis

- 100 ºC Oxygen and Nickel widely distributed
- 500 ºC Compressed layer and organic matter loss

Film

The region of 534-532 eV usually illustrates organic adsorbate species [4]:

-COH	(532.7 ± 0.2 eV)
-COO-	(532.1 ± 0.3 eV, 533.6 ± 0.1 eV)
-CO	(532.1 ± 0.1 eV)

Organic matter presence
Region from 532 to 534 eV

Being close to E_F
Presence of nickel oxide

Film

Suitable conditions

- MEA (stabilizer)
- 2-methoxyethanol
- Concentration 0.45 M
- Spin-rate 1000 rpm
- Anneling
  - 30 min
  - 100 ºC

OER Values

- η = 280 mV
- Tafel Slope = 45 mV dec^{-1}

Conclusions Further work

We report solution-processed NiOx ultra thin films (under 100 nm thickness) prepared by one-step procedure. These layers were prepared at mild temperatures. XPS and TGA show that organic matter still remaining on films after baking. This is also in agreement with HR-TEM images. As a result, the active surface area increases. XRD measured with HR-TEM shows the formation of cubic phase (bunsenite) of NiO nanocrystals.

The electrochemical performance of NiO_x thin films exhibits an outstanding overpotential values comparing with literature [3] for OER electrocatalysts.

Further work will include:

- Test the same material but used as HER electrode.
- Addition of other metals to enhance its light response.
- XPS comparison between NiO_x before and after CVs.
- Other material exploration for sol-gel@spin-coating synthesis.

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LOW-COST PRINTABLE METAL OXIDES FOR ELECTROCATALYSIS

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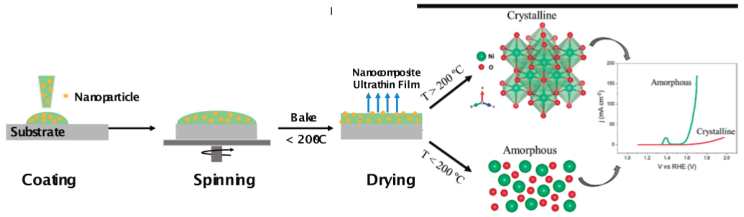
Herein, we present the recent progress in solution-processed NiOx thin films as a development of novel nanomaterials for electrocatalysis. In this work we also report our methodology to build ultrathin film layers based on sol-gel synthesis coupled by spin-coating [2] and adopted with a mild annealing process on a hot-plate (Fig 1). NiOx thin films are in-situ synthesized after deposition during a bake in a single step. The resulting film looks homogeneous without cracks nor pinholes. Our study demonstrated that NiOx films exhibit significantly enhanced electrocatalytic properties in comparison with bibliography results [3]. The most encouraging results were for NiOx films baked at low temperatures (below 150 oC) showing the best results regarding overpotential (h) for OER reaction.

We believe that our advances in solution-processed NiOx thin films baked at mild temperatures, may form the basis of a new platform for the fabrication of flexible devices with potential applications in light-driven water splitting and solar fuel cells.



non-stoichiometric NiOx films.

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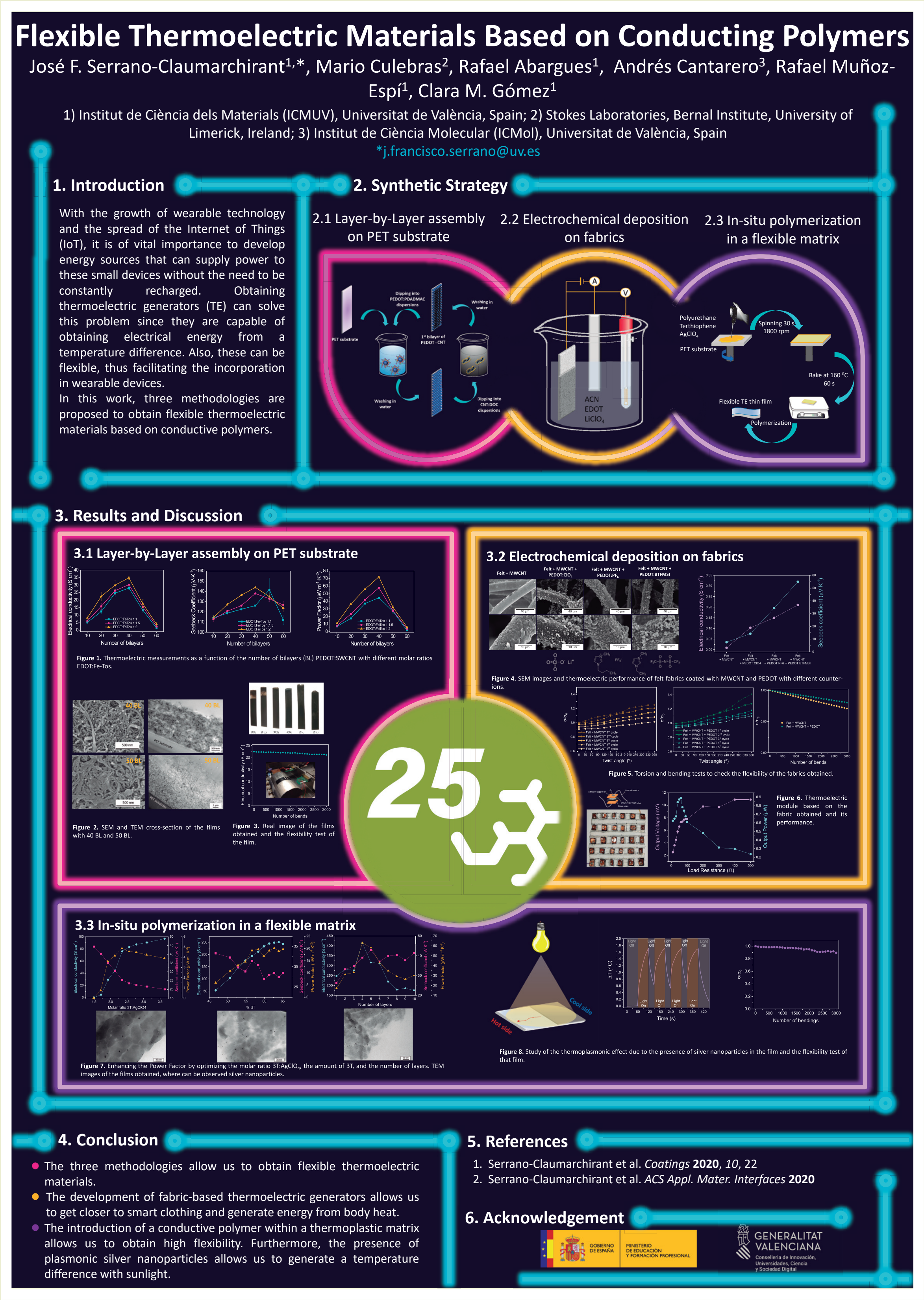

Flexible Thermoelectric Materials Based on Conducting Polymers

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1. Introduction

With the growth of wearable technology and the spread of the Internet of Things (IoT), it is of vital importance to develop energy sources that can supply power to these small devices without the need to be constantly recharged. Obtaining thermoelectric generators (TE) can solve this problem since they are capable of obtaining electrical energy from a temperature difference. Also, these can be flexible, thus facilitating the incorporation in wearable devices.

In this work, three methodologies are proposed to obtain flexible thermoelectric materials based on conductive polymers.

2. Synthetic Strategy

2.1 Layer-by-Layer assembly on PET substrate

2.2 Electrochemical deposition on fabrics

2.3 In-situ polymerization in a flexible matrix

3. Results and Discussion

3.1 Layer-by-Layer assembly on PET substrate

Figure 1. Thermoelectric measurements as a function of the number of bilayers (BL) PEDOT:SWCNT with different molar ratios EDOT:Fe-Tos.

Figure 2. SEM and TEM cross-section of the films with 40 BL and 50 BL.

Figure 3. Real image of the films obtained and the flexibility test of the film.

3.2 Electrochemical deposition on fabrics

Figure 4. SEM images and thermoelectric performance of felt fabrics coated with MWCNT and PEDOT with different counter-ions.

Figure 5. Torsion and bending tests to check the flexibility of the fabrics obtained.

Figure 6. Thermoelectric module based on the fabric obtained and its performance.

3.3 In-situ polymerization in a flexible matrix

Figure 7. Enhancing the Power Factor by optimizing the molar ratio 3T:$AgClO_4$, the amount of 3T, and the number of layers. TEM images of the films obtained, where can be observed silver nanoparticles.

Figure 8. Study of the thermoplasmonic effect due to the presence of silver nanoparticles in the film and the flexibility test of that film.

4. Conclusion

- The three methodologies allow us to obtain flexible thermoelectric materials.
- The development of fabric-based thermoelectric generators allows us to get closer to smart clothing and generate energy from body heat.
- The introduction of a conductive polymer within a thermoplastic matrix allows us to obtain high flexibility. Furthermore, the presence of plasmonic silver nanoparticles allows us to generate a temperature difference with sunlight.

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6. Acknowledgement

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FLEXIBLE THERMOELECTRIC MATERIALS BASED ON CONDUCTING POLYMERS

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With the recent development of wearable technology, the interest in flexible electronics, Internet of things (IoT), and self-powered electronic devices has increased, with the aim of achieving energy autonomy using portable and flexible power generation modules. In this sense, thermoelectric materials based on conductive polymers can be very good candidates for applications in wearable self-powered electronics due to their low thermal conductivity, low cost, eco-friendly, processing versatility, and mechanical flexibility.

There are several ways to process flexible materials. In this work, we present three ways of depositing flexible thermoelectric materials based on conductive polymers; they use different deposition techniques on different substrates, highlighting the great versatility of these materials. First, by using the layer-by-layer technique, successive layers of PEDOT nanoparticles and carbon nanotubes are deposited on a flexible PET substrate.1 In the second work, by combining layer-by-layer techniques and electrochemical deposition, highly flexible fabrics coated with carbon nanotubes and PEDOT: ClO4 are obtained.2 Finally, by means of the spin coating technique, it has been possible to embed polythiophene (PTP) within a thermoplastic polyurethane matrix by means of chemical oxidation in the presence of different oxidizing metal salts.

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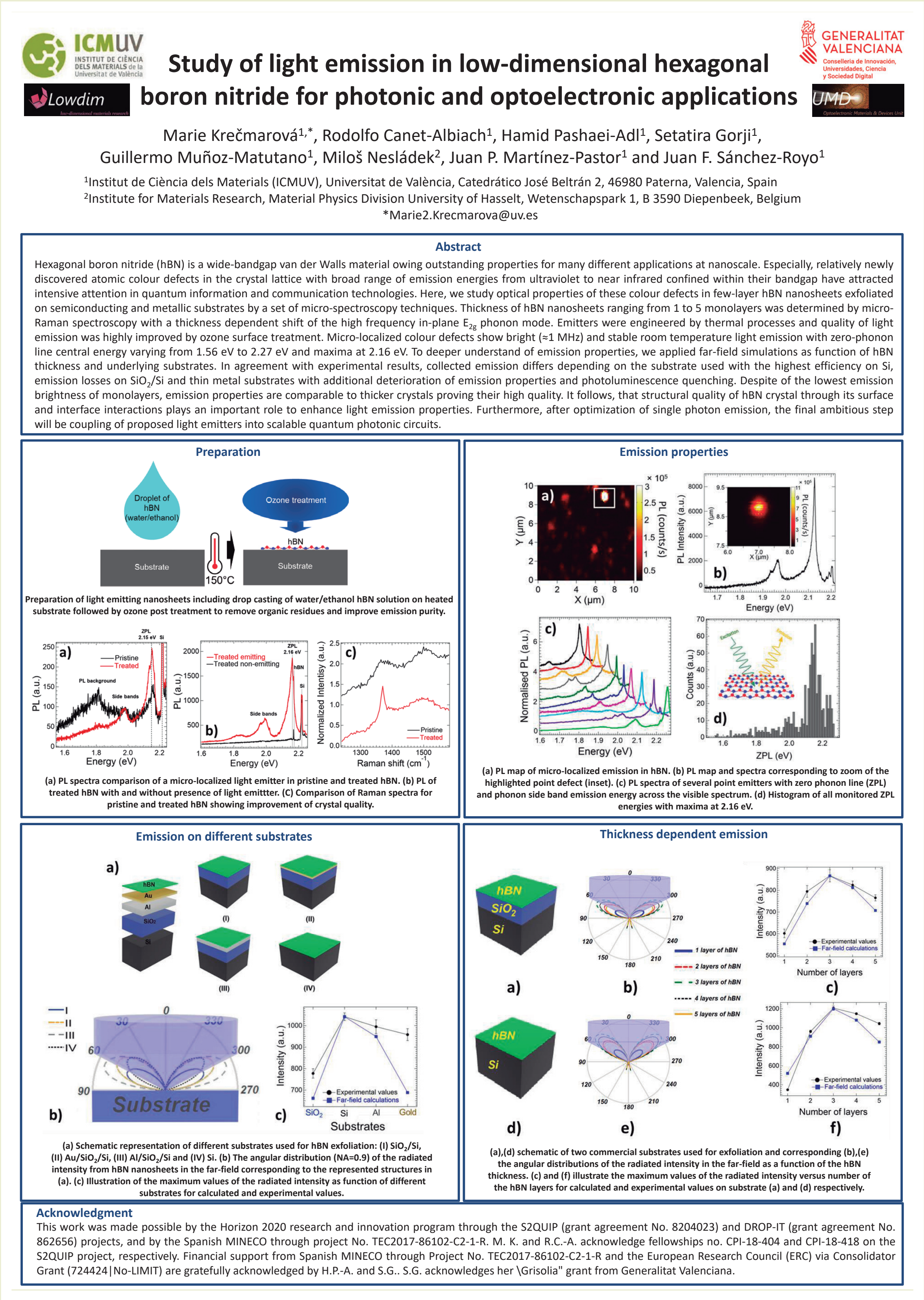

Study of light emission in low-dimensional hexagonal boron nitride for photonic and optoelectronic applications

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Abstract

Hexagonal boron nitride (hBN) is a wide-bandgap van der Walls material owing outstanding properties for many different applications at nanoscale. Especially, relatively newly discovered atomic colour defects in the crystal lattice with broad range of emission energies from ultraviolet to near infrared confined within their bandgap have attracted intensive attention in quantum information and communication technologies. Here, we study optical properties of these colour defects in few-layer hBN nanosheets exfoliated on semiconducting and metallic substrates by a set of micro-spectroscopy techniques. Thickness of hBN nanosheets ranging from 1 to 5 monolayers was determined by micro-Raman spectroscopy with a thickness dependent shift of the high frequency in-plane E_{2g} phonon mode. Emitters were engineered by thermal processes and quality of light emission was highly improved by ozone surface treatment. Micro-localized colour defects show bright (≈1 MHz) and stable room temperature light emission with zero-phonon line central energy varying from 1.56 eV to 2.27 eV and maxima at 2.16 eV. To deeper understand of emission properties, we applied far-field simulations as function of hBN thickness and underlying substrates. In agreement with experimental results, collected emission differs depending on the substrate used with the highest efficiency on Si, emission losses on SiO_2/Si and thin metal substrates with additional deterioration of emission properties and photoluminescence quenching. Despite of the lowest emission brightness of monolayers, emission properties are comparable to thicker crystals proving their high quality. It follows, that structural quality of hBN crystal through its surface and interface interactions plays an important role to enhance light emission properties. Furthermore, after optimization of single photon emission, the final ambitious step will be coupling of proposed light emitters into scalable quantum photonic circuits.

Preparation

Preparation of light emitting nanosheets including drop casting of water/ethanol hBN solution on heated substrate followed by ozone post treatment to remove organic residues and improve emission purity.

(a) PL spectra comparison of a micro-localized light emitter in pristine and treated hBN. (b) PL of treated hBN with and without presence of light emittter. (C) Comparison of Raman spectra for pristine and treated hBN showing improvement of crystal quality.

Emission properties

(a) PL map of micro-localized emission in hBN. (b) PL map and spectra corresponding to zoom of the highlighted point defect (inset). (c) PL spectra of several point emitters with zero phonon line (ZPL) and phonon side band emission energy across the visible spectrum. (d) Histogram of all monitored ZPL energies with maxima at 2.16 eV.

Emission on different substrates

(a) Schematic representation of different substrates used for hBN exfoliation: (I) SiO_2/Si, (II) Au/SiO_2/Si, (III) Al/SiO_2/Si and (IV) Si. (b) The angular distribution (NA=0.9) of the radiated intensity from hBN nanosheets in the far-field corresponding to the represented structures in (a). (c) Illustration of the maximum values of the radiated intensity as function of different substrates for calculated and experimental values.

Thickness dependent emission

(a),(d) schematic of two commercial substrates used for exfoliation and corresponding (b),(e) the angular distributions of the radiated intensity in the far-field as a function of the hBN thickness. (c) and (f) illustrate the maximum values of the radiated intensity versus number of the hBN layers for calculated and experimental values on substrate (a) and (d) respectively.

Acknowledgment

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STUDY OF LIGHT EMISSION IN LOW-DIMENSIONAL

HEXAGONAL BORON NITRIDE FOR PHOTONIC AND OPTOELECTRONIC APPLICATIONS

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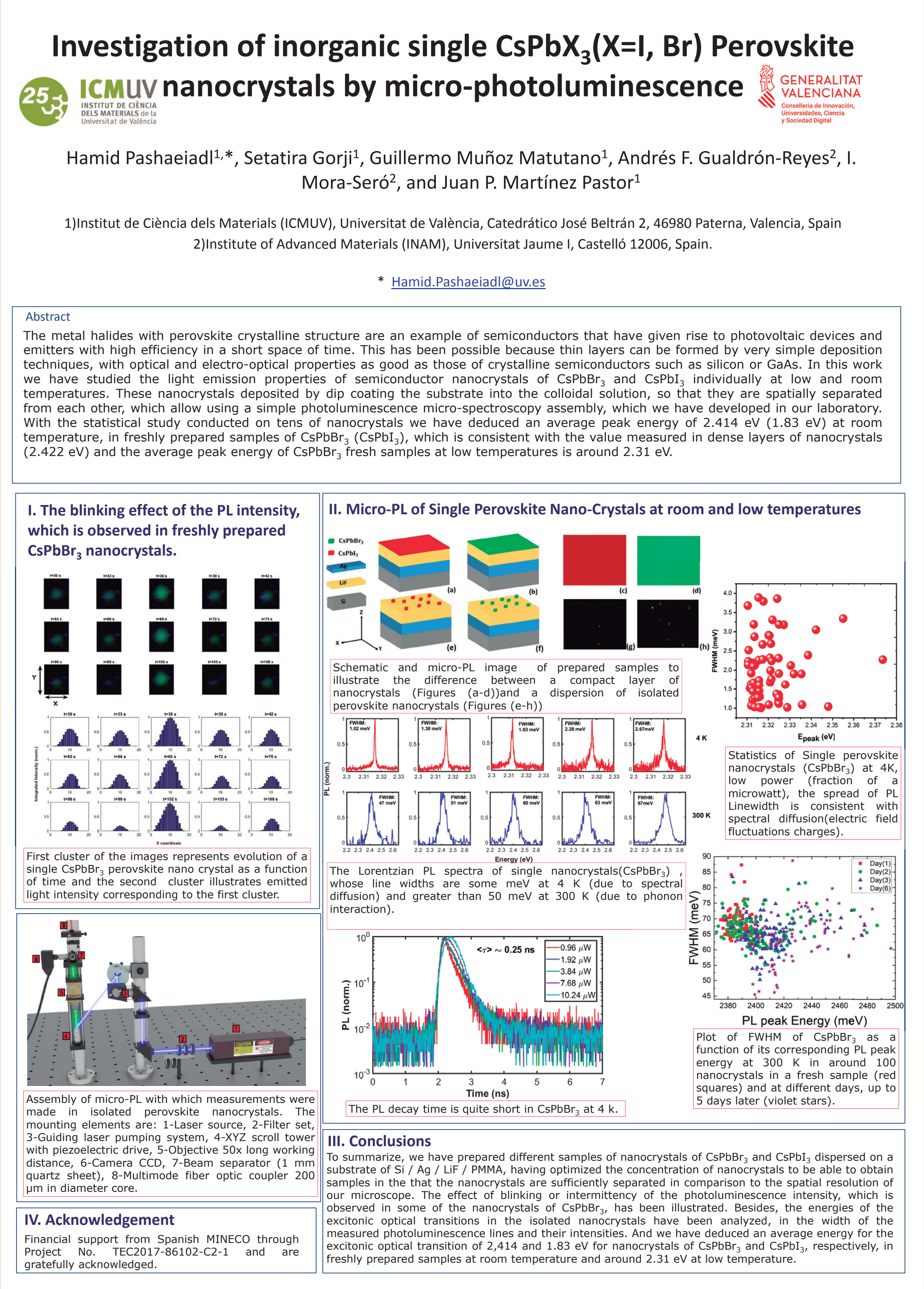
Hexagonal boron nitride (hBN) is a wide-bandgap van der Walls material owing outstanding properties for many different applications at nanoscale. Especially, relatively newly discovered atomic colour defects in the crystal lattice with broad range of emission energies from ultraviolet to near infrared confined within their bandgap have attracted intensive attention in quantum information and communication technologies. Here, we study optical properties of these colour defects in few-layer hBN nanosheets exfoliated on semiconducting and metallic substrates by a set of micro-spectroscopy techniques. Thickness of hBN nanosheets ranging from 1 to 5 monolayers was determined by micro-Raman spectroscopy with a thickness dependent shift of the high frequency in-plane E2g phonon mode. Emitters were engineered by thermal processes and quality of light emission was highly improved by ozone surface treatment. Micro-localized colour defects show bright (≈1 MHz) and stable room temperature light emission with zero-phonon line central energy varying from 1.56 eV to 2.27 eV and maxima at 2.16 eV. To deeper understand of emission properties, we applied far-field simulations as function of hBN thickness and underlying substrates. In agreement with experimental results, collected emission differs depending on the substrate used with the highest efficiency on Si, emission losses on SiO2/Si and thin metal substrates with additional deterioration of emission properties and photoluminescence quenching. Despite of the lowest emission brightness of monolayers, emission properties are comparable to thicker crystals proving their high quality. It follows, that structural quality of hBN crystal through its surface and interface interactions plays an important role to enhance light emission properties. Furthermore, after optimization of single photon emission, the final ambitious step will be coupling of proposed light emitters into scalable quantum photonic circuits.



Investigation of inorganic single $CsPbX_3$(X=I, Br) Perovskite nanocrystals by micro-photoluminescence

Hamid Pashaeiadl[1,*], Setatira Gorji[1], Guillermo Muñoz Matutano[1], Andrés F. Gualdrón-Reyes[2], I. Mora-Seró[2], and Juan P. Martínez Pastor[1]

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Abstract

The metal halides with perovskite crystalline structure are an example of semiconductors that have given rise to photovoltaic devices and emitters with high efficiency in a short space of time. This has been possible because thin layers can be formed by very simple deposition techniques, with optical and electro-optical properties as good as those of crystalline semiconductors such as silicon or GaAs. In this work we have studied the light emission properties of semiconductor nanocrystals of $CsPbBr_3$ and $CsPbI_3$ individually at low and room temperatures. These nanocrystals deposited by dip coating the substrate into the colloidal solution, so that they are spatially separated from each other, which allow using a simple photoluminescence micro-spectroscopy assembly, which we have developed in our laboratory. With the statistical study conducted on tens of nanocrystals we have deduced an average peak energy of 2.414 eV (1.83 eV) at room temperature, in freshly prepared samples of $CsPbBr_3$ ($CsPbI_3$), which is consistent with the value measured in dense layers of nanocrystals (2.422 eV) and the average peak energy of $CsPbBr_3$ fresh samples at low temperatures is around 2.31 eV.

I. The blinking effect of the PL intensity, which is observed in freshly prepared $CsPbBr_3$ nanocrystals.

First cluster of the images represents evolution of a single $CsPbBr_3$ perovskite nano crystal as a function of time and the second cluster illustrates emitted light intensity corresponding to the first cluster.

Assembly of micro-PL with which measurements were made in isolated perovskite nanocrystals. The mounting elements are: 1-Laser source, 2-Filter set, 3-Guiding laser pumping system, 4-XYZ scroll tower with piezoelectric drive, 5-Objective 50x long working distance, 6-Camera CCD, 7-Beam separator (1 mm quartz sheet), 8-Multimode fiber optic coupler 200 µm in diameter core.

II. Micro-PL of Single Perovskite Nano-Crystals at room and low temperatures

Schematic and micro-PL image of prepared samples to illustrate the difference between a compact layer of nanocrystals (Figures (a-d))and a dispersion of isolated perovskite nanocrystals (Figures (e-h))

Statistics of Single perovskite nanocrystals ($CsPbBr_3$) at 4K, low power (fraction of a microwatt), the spread of PL Linewidth is consistent with spectral diffusion(electric field fluctuations charges).

The Lorentzian PL spectra of single nanocrystals($CsPbBr_3$) , whose line widths are some meV at 4 K (due to spectral diffusion) and greater than 50 meV at 300 K (due to phonon interaction).

Plot of FWHM of $CsPbBr_3$ as a function of its corresponding PL peak energy at 300 K in around 100 nanocrystals in a fresh sample (red squares) and at different days, up to 5 days later (violet stars).

The PL decay time is quite short in $CsPbBr_3$ at 4 k.

III. Conclusions

To summarize, we have prepared different samples of nanocrystals of $CsPbBr_3$ and $CsPbI_3$ dispersed on a substrate of Si / Ag / LiF / PMMA, having optimized the concentration of nanocrystals to be able to obtain samples in the that the nanocrystals are sufficiently separated in comparison to the spatial resolution of our microscope. The effect of blinking or intermittency of the photoluminescence intensity, which is observed in some of the nanocrystals of $CsPbBr_3$, has been illustrated. Besides, the energies of the excitonic optical transitions in the isolated nanocrystals have been analyzed, in the width of the measured photoluminescence lines and their intensities. And we have deduced an average energy for the excitonic optical transition of 2,414 and 1.83 eV for nanocrystals of $CsPbBr_3$ and $CsPbI_3$, respectively, in freshly prepared samples at room temperature and around 2.31 eV at low temperature.

IV. Acknowledgement

Financial support from Spanish MINECO through Project No. TEC2017-86102-C2-1 and are gratefully acknowledged.

INVESTIGATION OF INORGANIC SINGLE CSPBX3(X=I, BR) PEROVSKITE NANOCRYSTALS BY MICRO-PHOTOLUMINESCENCE

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The metal halides with perovskite crystalline structure are an example of semiconductors that have given rise to photovoltaic devices and emitters with high efficiency in a short space of time [1-3]. This has been possible because thin layers can be formed by very simple deposition techniques, with optical and electro-optical properties as good as those of crystalline semiconductors such as silicon or GaAs. In this work we have studied the light emission properties of semiconductor nanocrystals of CsPbBr3 and CsPbI3 individually at low and room temperatures. These nanocrystals deposited by dip coating the substrate into the colloidal solution, so that they are spatially separated from each other, which allow using a simple photoluminescence micro-spectroscopy assembly, which we have developed in our laboratory. With the statistical study conducted on tens of nanocrystals we have deduced an average peak energy of 2,414 eV (1.83 eV) at room temperature, in freshly prepared samples of CsPbBr3 (CsPbI3), which is consistent with the value measured in dense layers of nanocrystals (2,422 eV) and the average peak energy of CsPbBr3 fresh samples at low temperatures is around 2,31 eV. The line width of the photoluminescence spectrum in these types of layers hardly differs from the value found in the isolated nanocrystals (on average), because the aforementioned width is greater than the dispersion in their peak energies at room temperatures. This dispersion in the energies of the fundamental excitonic transition in the studied nanocrystals is due to the dispersion of their sizes.

References:

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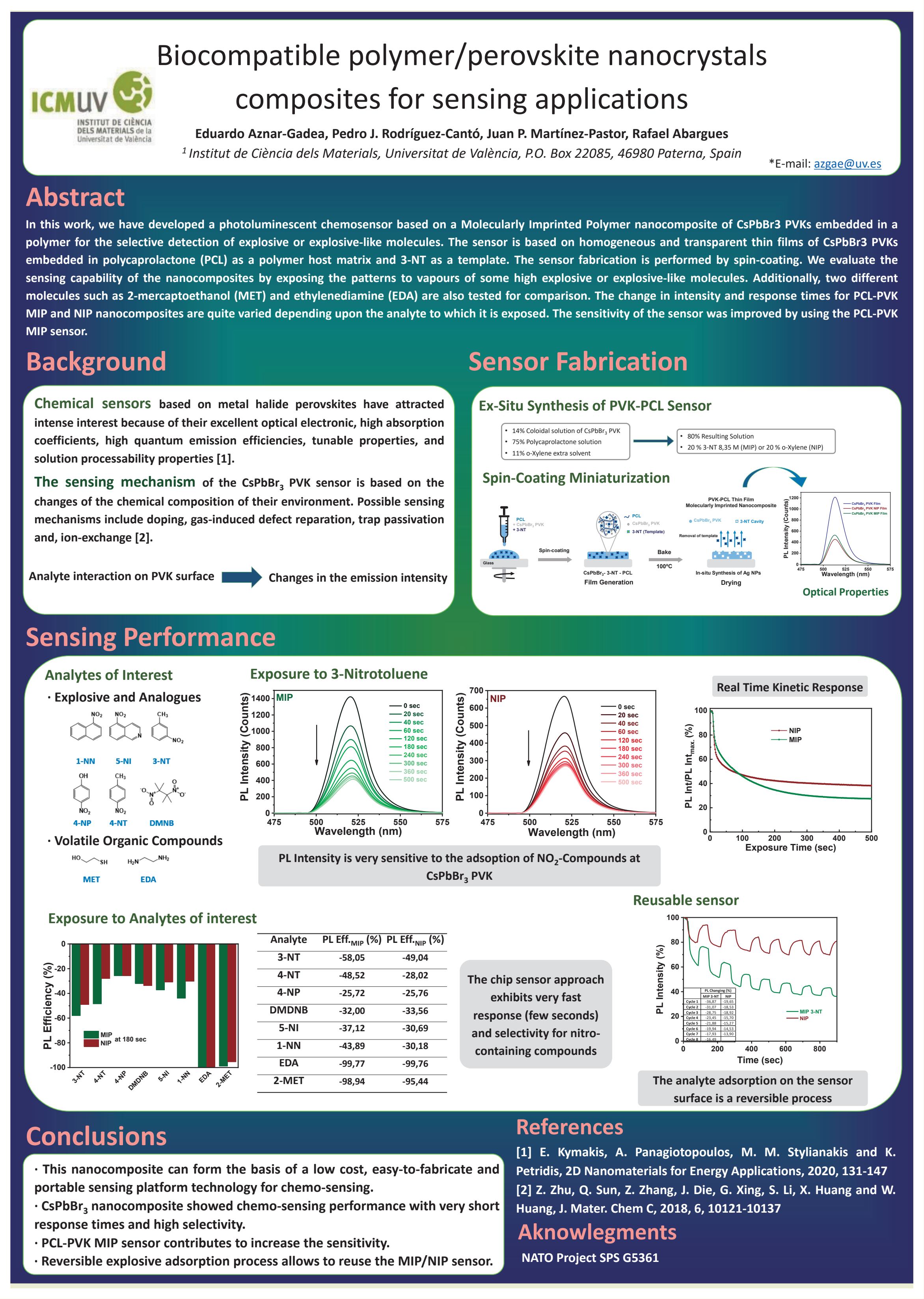
[3] Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of cesium lead halide perovskites (CsPbX3, X= Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. Nano letters, 2015, 15, 3692-3696.



Biocompatible polymer/perovskite nanocrystals composites for sensing applications

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Abstract

In this work, we have developed a photoluminescent chemosensor based on a Molecularly Imprinted Polymer nanocomposite of CsPbBr3 PVKs embedded in a polymer for the selective detection of explosive or explosive-like molecules. The sensor is based on homogeneous and transparent thin films of CsPbBr3 PVKs embedded in polycaprolactone (PCL) as a polymer host matrix and 3-NT as a template. The sensor fabrication is performed by spin-coating. We evaluate the sensing capability of the nanocomposites by exposing the patterns to vapours of some high explosive or explosive-like molecules. Additionally, two different molecules such as 2-mercaptoethanol (MET) and ethylenediamine (EDA) are also tested for comparison. The change in intensity and response times for PCL-PVK MIP and NIP nanocomposites are quite varied depending upon the analyte to which it is exposed. The sensitivity of the sensor was improved by using the PCL-PVK MIP sensor.

Background

Chemical sensors based on metal halide perovskites have attracted intense interest because of their excellent optical electronic, high absorption coefficients, high quantum emission efficiencies, tunable properties, and solution processability properties [1].

The sensing mechanism of the $CsPbBr_3$ PVK sensor is based on the changes of the chemical composition of their environment. Possible sensing mechanisms include doping, gas-induced defect reparation, trap passivation and, ion-exchange [2].

Analyte interaction on PVK surface → Changes in the emission intensity

Sensor Fabrication

Ex-Situ Synthesis of PVK-PCL Sensor

- 14% Coloidal solution of $CsPbBr_3$ PVK
- 75% Polycaprolactone solution
- 11% o-Xylene extra solvent

→

- 80% Resulting Solution
- 20 % 3-NT 8,35 M (MIP) or 20 % o-Xylene (NIP)

Spin-Coating Miniaturization

Sensing Performance

Analytes of Interest

- Explosive and Analogues

- Volatile Organic Compounds

Exposure to 3-Nitrotoluene

PL Intensity is very sensitive to the adsoption of NO_2-Compounds at $CsPbBr_3$ PVK

Real Time Kinetic Response

Exposure to Analytes of interest

Analyte	PL $Eff._{MIP}$ (%)	PL $Eff._{NIP}$ (%)
3-NT	-58,05	-49,04
4-NT	-48,52	-28,02
4-NP	-25,72	-25,76
DMDNB	-32,00	-33,56
5-NI	-37,12	-30,69
1-NN	-43,89	-30,18
EDA	-99,77	-99,76
2-MET	-98,94	-95,44

The chip sensor approach exhibits very fast response (few seconds) and selectivity for nitro-containing compounds

Reusable sensor

	MIP 3-NT	NIP
Cycle 1	-36,87	-19,65
Cycle 2	-31,07	-18,53
Cycle 3	-28,75	-18,92
Cycle 4	-23,45	-15,70
Cycle 5	-21,88	-15,27
Cycle 6	-19,94	-14,53
Cycle 7	-17,93	-13,90
Cycle 8	-16,49	

The analyte adsorption on the sensor surface is a reversible process

Conclusions

- This nanocomposite can form the basis of a low cost, easy-to-fabricate and portable sensing platform technology for chemo-sensing.
- $CsPbBr_3$ nanocomposite showed chemo-sensing performance with very short response times and high selectivity.
- PCL-PVK MIP sensor contributes to increase the sensitivity.
- Reversible explosive adsorption process allows to reuse the MIP/NIP sensor.

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[1] E. Kymakis, A. Panagiotopoulos, M. M. Stylianakis and K. Petridis, 2D Nanomaterials for Energy Applications, 2020, 131-147
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Aknowlegments

NATO Project SPS G5361

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BIOCOMPATIBLE POLYMER/PEROVSKITE NANOCRYSTALS COMPOSITES FOR SENSING APPLICATIONS

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Chemical sensors based on lead halide perovskite nanocrystals (NCs) have attracted intense interest because of their excellent optical electronic, high absorption coefficients, high quantum emission efficiencies, tunable properties, and solution processability properties [1]. The sensing mechanism of the CsPbBr3 NCs sensor is based on the changes of the chemical composition of their surroundings. Possible sensing mechanisms include doping, gas-induced defect reparation, trap passivation and, ion-exchange [2].

In this work, we have developed a photoluminescent chemosensor based on a molecularly imprinted polymer (MIP) nanocomposite of CsPbBr3 NCs embedded in a polymer for the selective detection of explosive or explosive-like molecules. Moreover, we synthesize non-molecularly imprinted polymers (NIP) to compare the results. The sensor is based on homogeneous and transparent thin films of CsPbBr3 NCs embedded in polycaprolactone (PCL) as a polymer host matrix and 3-nitrotoluene (3-NT) as a template.

We evaluate the sensing capability of MIP and NIP nanocomposites by exposing the thin films to vapours of some explosive taggants. There are molecules that show moderate vapour pressures and slowly evaporate from the explosive. The addition of these compounds is required in all legally manufactured explosives. Additionally, two volatile organic compounds such as 2-mercaptoethanol (MET) and ethylenediamine (EDA) are also tested for comparison. We observe that the change in intensity and response times for MIP and NIP nanocomposites depend on the analyte to which it is exposed. We demonstrate an enhanced sensing performance when MIP approach is used.

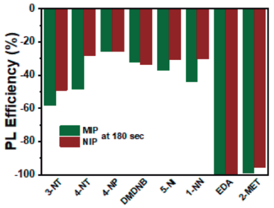
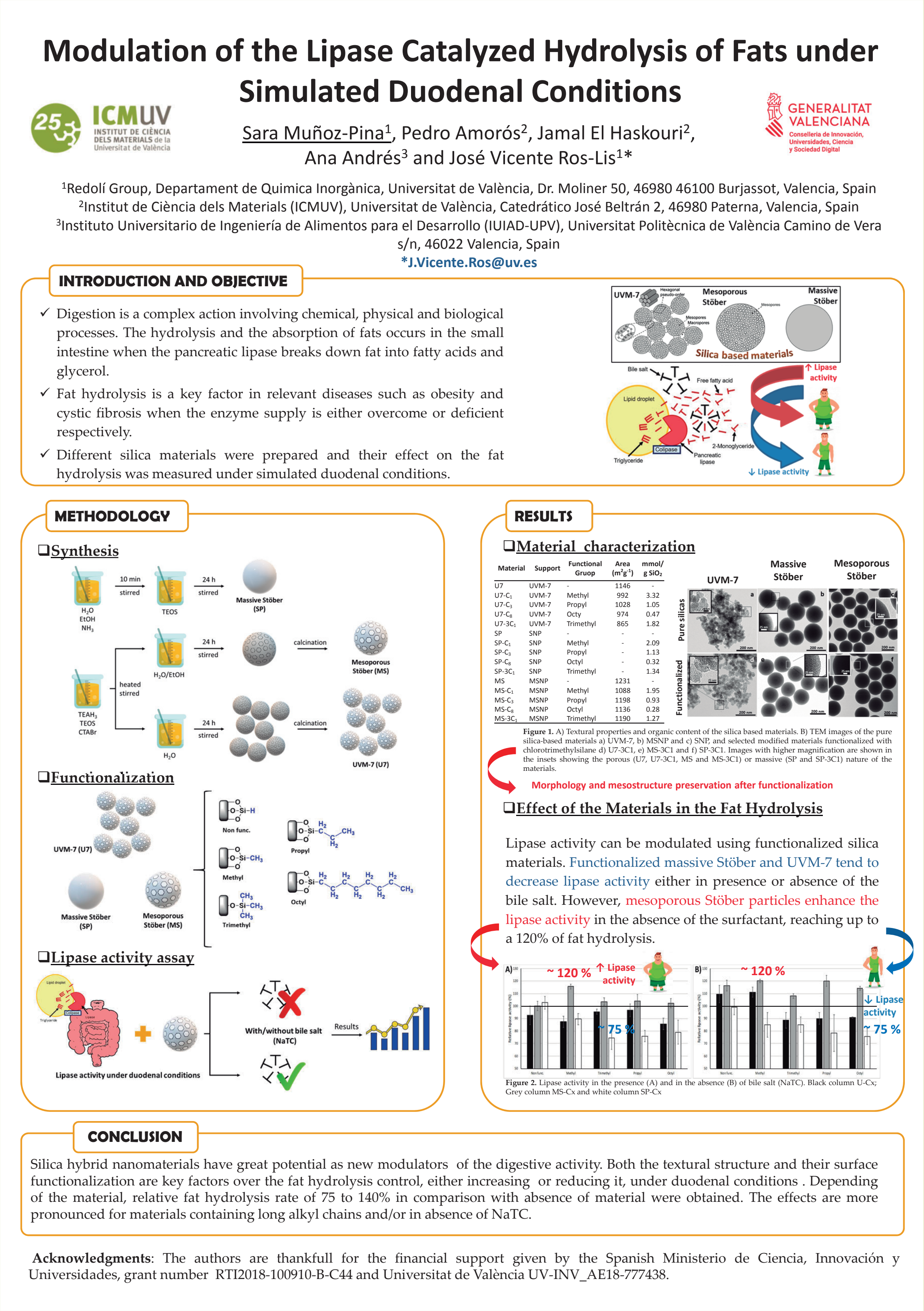


Figure 1. Selectivity of CsPbBr3-PCL MIP/NIP sensor to 3-NT, 4-NT, 4-NP, DMDNB, 5-NI, 1-NN, EDA and 2-MET.

[1] E. Kymakis, A. Panagiotopoulos, M. M. Stylianakis and K. Petridis, 2D Nanomaterials for Energy Applications, 2020, 131-147

[2] Z. Zhu, Q. Sun, Z. Zhang, J. Die, G. Xing, S. Li, X. Huang and W. Huang, J. Mater. Chem C, 2018, 6, 10121-10137



Modulation of the Lipase Catalyzed Hydrolysis of Fats under Simulated Duodenal Conditions

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INTRODUCTION AND OBJECTIVE

- ✓ Digestion is a complex action involving chemical, physical and biological processes. The hydrolysis and the absorption of fats occurs in the small intestine when the pancreatic lipase breaks down fat into fatty acids and glycerol.
- ✓ Fat hydrolysis is a key factor in relevant diseases such as obesity and cystic fibrosis when the enzyme supply is either overcome or deficient respectively.
- ✓ Different silica materials were prepared and their effect on the fat hydrolysis was measured under simulated duodenal conditions.

METHODOLOGY

❑Synthesis

❑Functionalization

❑Lipase activity assay

RESULTS

❑Material characterization

Material	Support	Functional Gruop	Area (m^{2}g^{-1})	mmol/ g SiO$_2$
U7	UVM-7	-	1146	-
U7-C$_1$	UVM-7	Methyl	992	3.32
U7-C$_3$	UVM-7	Propyl	1028	1.05
U7-C$_8$	UVM-7	Octy	974	0.47
U7-3C$_1$	UVM-7	Trimethyl	865	1.82
SP	SNP	-	-	-
SP-C$_1$	SNP	Methyl	-	2.09
SP-C$_3$	SNP	Propyl	-	1.13
SP-C$_8$	SNP	Octyl	-	0.32
SP-3C$_1$	SNP	Trimethyl	-	1.34
MS	MSNP	-	1231	-
MS-C$_1$	MSNP	Methyl	1088	1.95
MS-C$_3$	MSNP	Propyl	1198	0.93
MS-C$_8$	MSNP	Octyl	1136	0.28
MS-3C$_1$	MSNP	Trimethyl	1190	1.27

Figure 1. A) Textural properties and organic content of the silica based materials. B) TEM images of the pure silica-based materials a) UVM-7, b) MSNP and c) SNP, and selected modified materials functionalized with chlorotrimethylsilane d) U7-3C1, e) MS-3C1 and f) SP-3C1. Images with higher magnification are shown in the insets showing the porous (U7, U7-3C1, MS and MS-3C1) or massive (SP and SP-3C1) nature of the materials.

Morphology and mesostructure preservation after functionalization

❑Effect of the Materials in the Fat Hydrolysis

Lipase activity can be modulated using functionalized silica materials. Functionalized massive Stöber and UVM-7 tend to decrease lipase activity either in presence or absence of the bile salt. However, mesoporous Stöber particles enhance the lipase activity in the absence of the surfactant, reaching up to a 120% of fat hydrolysis.

Figure 2. Lipase activity in the presence (A) and in the absence (B) of bile salt (NaTC). Black column U-Cx; Grey column MS-Cx and white column SP-Cx

CONCLUSION

Silica hybrid nanomaterials have great potential as new modulators of the digestive activity. Both the textural structure and their surface functionalization are key factors over the fat hydrolysis control, either increasing or reducing it, under duodenal conditions . Depending of the material, relative fat hydrolysis rate of 75 to 140% in comparison with absence of material were obtained. The effects are more pronounced for materials containing long alkyl chains and/or in absence of NaTC.

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MODULATION OF THE LIPASE CATALYZED HYDROLYSIS OF FATS UNDER SIMULATED DUODENAL CONDITIONS

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Digestion is a complex action involving chemical, physical and biological processes [1]. Most of the hydrolysis of fats and their absorption occurs in the small intestine. When fat reaches the small intestine, it is normally in the form of globules, which size depends on numerous factors such as the type of fat, the presence of other substances, the mixing time etc. The effect of silica materials and their functionalization in the lipase catalyzed fat hydrolysis has been scarcely studied. Different silica materials were prepared and their effect on the fat hydrolysis was measured, under simulated duodenal conditions. The materials are composed of the combination of three supports (Stöber massive silica nanoparticles (SM), Stöber mesoporous nanoparticles (SMP) and UVM-7) and four surface functionalizations (methyl, trimethyl, propyl and octyl). The functional groups were selected to offer a hydrophobic character to the material improving the interaction with the fat globules and the lipase. Depending of the material, relative fat hydrolysis rates of 75 to 140% in comparison with absence of the material were obtained. The results were analyzed by Partial Least Square Regression and suggest that the alkyl modified mesopores are able to improve the fat hydrolysis, by contrast the non-porous nanoparticles and the textural pores tend to induce inhibition. The effects are more pronounced for materials containing long alkyl chains and/or in absence of taurodeoxycholate.

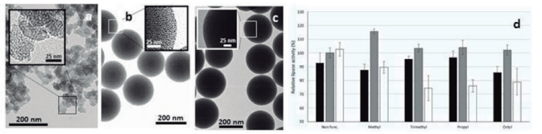
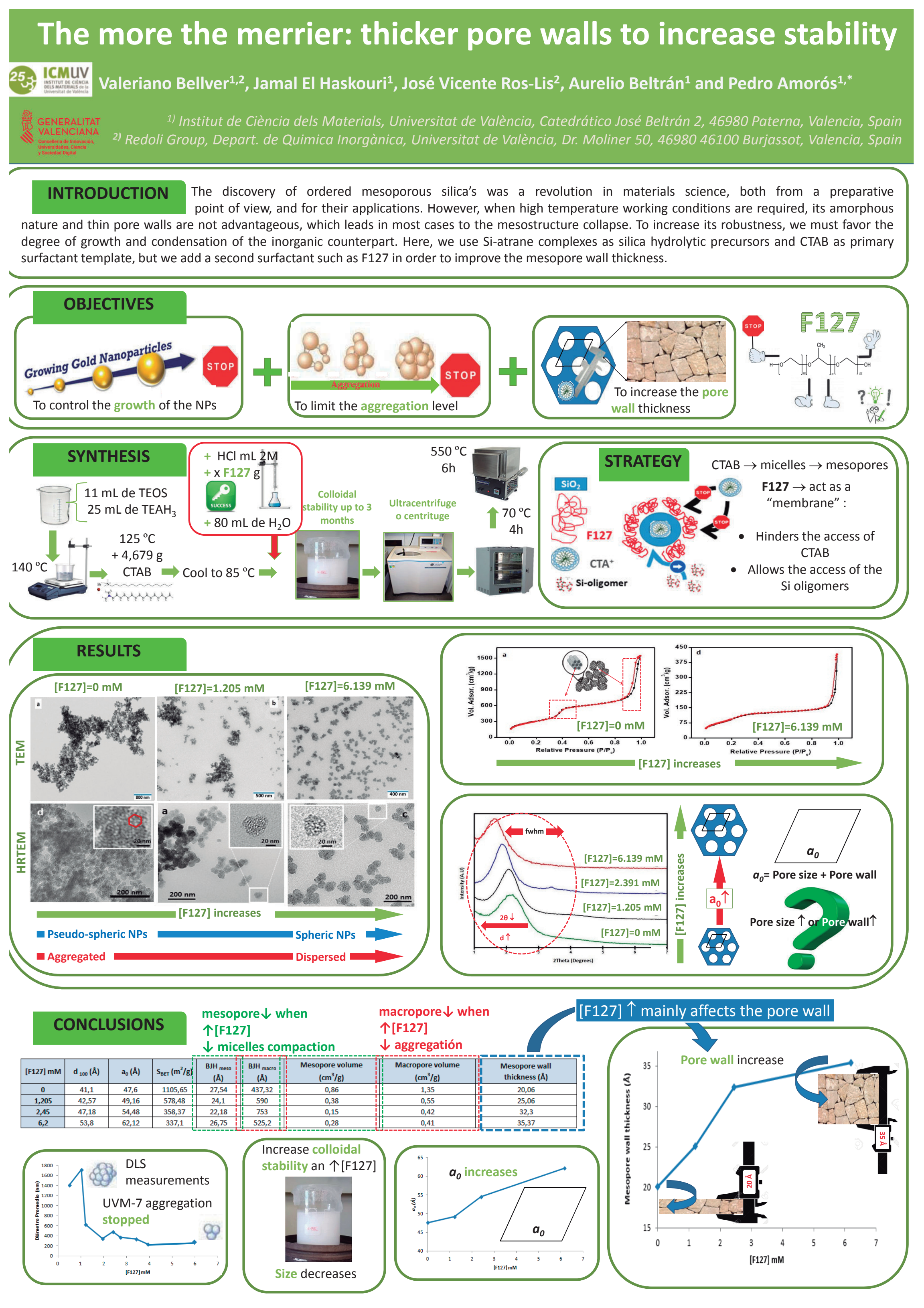


Figure 1: TEM images of (a) UVM-7, (b) SMP and (c) SM silicas. (d) Lipase activity in the presence of bile salt. Black grey and white columns correspond to UVM-7, SMP and SM, respectively.

[1] Use of Silica Based Materials as Modulators of the Lipase Catalyzed Hydrolysis of Fats under Simulated Duodenal Conditions S. Muñoz-Pina et al., Nanomaterials 2020, 10, 1927; doi:10.3390/nano10101927



The more the merrier: thicker pore walls to increase stability

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INTRODUCTION The discovery of ordered mesoporous silica's was a revolution in materials science, both from a preparative point of view, and for their applications. However, when high temperature working conditions are required, its amorphous nature and thin pore walls are not advantageous, which leads in most cases to the mesostructure collapse. To increase its robustness, we must favor the degree of growth and condensation of the inorganic counterpart. Here, we use Si-atrane complexes as silica hydrolytic precursors and CTAB as primary surfactant template, but we add a second surfactant such as F127 in order to improve the mesopore wall thickness.

OBJECTIVES

To control the growth of the NPs + To limit the aggregation level + To increase the pore wall thickness

SYNTHESIS

11 mL de TEOS
25 mL de TEAH$_3$
140 °C → 125 °C + 4,679 g CTAB → Cool to 85 °C → + HCl mL 2M + x F127 g + 80 mL de H_2O → Colloidal stability up to 3 months → Ultracentrifuge o centritruge → 70 °C 4h → 550 °C 6h

STRATEGY

CTAB → micelles → mesopores
F127 → act as a "membrane" :
- Hinders the access of CTAB
- Allows the access of the Si oligomers

RESULTS

CONCLUSIONS

mesopore↓ when ↑[F127] ↓ micelles compaction

macropore↓ when ↑[F127] ↓ aggregatión

[F127] ↑ mainly affects the pore wall

[F127] mM	d_{100} (Å)	a_0 (Å)	S_{BET} (m^2/g)	BJH meso (Å)	BJH macro (Å)	Mesopore volume (cm^3/g)	Macropore volume (cm^3/g)	Mesopore wall thickness (Å)
0	41,1	47,6	1105,65	27,54	437,32	0,86	1,35	20,06
1,205	42,57	49,16	578,48	24,1	590	0,38	0,55	25,06
2,45	47,18	54,48	358,37	22,18	753	0,15	0,42	32,3
6,2	53,8	62,12	337,1	26,75	525,2	0,28	0,41	35,37

DLS measurements
UVM-7 aggregation stopped

Increase colloidal stability an ↑[F127]
Size decreases

a_0 increases

Pore wall increase

THE MORE THE MERRIER: THICKER PORE WALLS TO INCREASE STABILITY

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The discovery of ordered mesoporous silicas was a milestone in the materials science field, not only from the preparative point of view, but also due to their applications. However, when high temperature conditions are required, their amorphous nature and thin pore walls imply a drawback due to the relative ease with which the mesostructure collapses. To increase its robustness, we must promote the growth and condensation of the inorganic skeleton. This facet has already been explored using a diversity of Si sources [1]. We have persisted in using silatranes as hydrolytic precursors of silica in synthesis assisted by CTAB as templating agent, but we have explored the effect of introducing in our preparative path a second surfactant such as F127 [2]. The role played by each surfactant is different (Figure 1a). The strong S+I- interactions with silica favour the functionality of CTAB as primary template able to generate cylindrical mesopores (after CTAB evolution). On the other hand, the milder interactions with silica and the amphiphilic nature of the block copolymers allow that F127 acts by blocking the access of the reagents, CTAB micelles and silica oligomers, to the nanoparticle's surface, what hinders a "normal" growth. However, the diffusion difficulties through F127 aggregates are lower for the silica oligomers than for the relatively large CTAB micelles. This sterictype access-selectivity favours the growth of the pore walls (Figure 1b). Furthermore, the F127 addition promotes high particle dispersion (Figure 1c), which remain as colloidal suspensions for months.

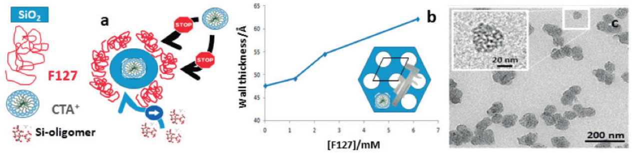

Figure 1: (a) Proposed reaction mechanism. (b) Pore wall thickness vs [F127]. (c) TEM image showing a high dispersion degree.

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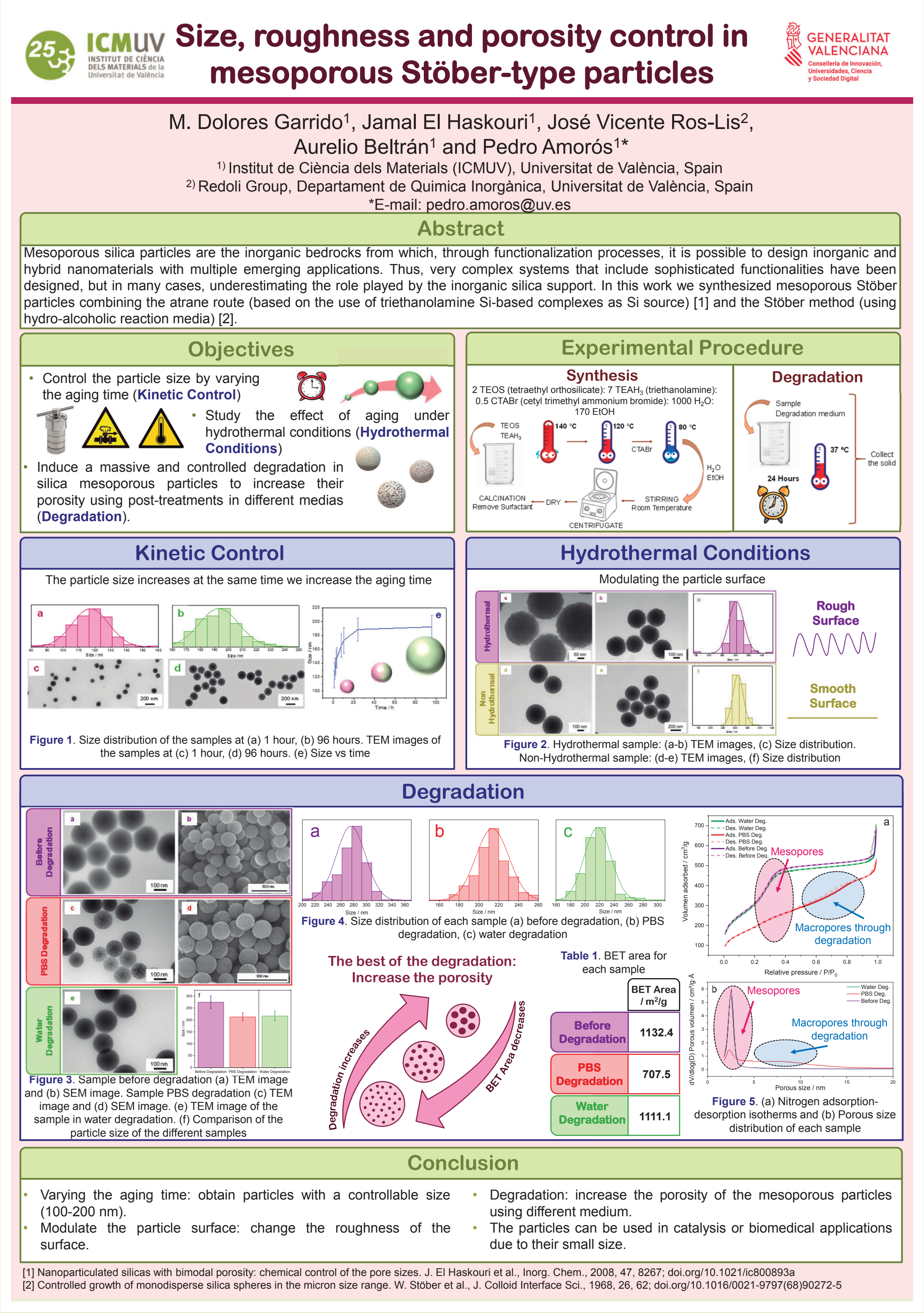

Size, roughness and porosity control in mesoporous Stöber-type particles

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Abstract

Mesoporous silica particles are the inorganic bedrocks from which, through functionalization processes, it is possible to design inorganic and hybrid nanomaterials with multiple emerging applications. Thus, very complex systems that include sophisticated functionalities have been designed, but in many cases, underestimating the role played by the inorganic silica support. In this work we synthesized mesoporous Stöber particles combining the atrane route (based on the use of triethanolamine Si-based complexes as Si source) [1] and the Stöber method (using hydro-alcoholic reaction media) [2].

Objectives

- Control the particle size by varying the aging time (**Kinetic Control**)
- Study the effect of aging under hydrothermal conditions (**Hydrothermal Conditions**)
- Induce a massive and controlled degradation in silica mesoporous particles to increase their porosity using post-treatments in different medias (**Degradation**).

Experimental Procedure

Synthesis

2 TEOS (tetraethyl orthosilicate): 7 $TEAH_3$ (triethanolamine): 0.5 CTABr (cetyl trimethyl ammonium bromide): 1000 H_2O: 170 EtOH

Degradation

Kinetic Control

The particle size increases at the same time we increase the aging time

Figure 1. Size distribution of the samples at (a) 1 hour, (b) 96 hours. TEM images of the samples at (c) 1 hour, (d) 96 hours. (e) Size vs time

Hydrothermal Conditions

Modulating the particle surface

Figure 2. Hydrothermal sample: (a-b) TEM images, (c) Size distribution. Non-Hydrothermal sample: (d-e) TEM images, (f) Size distribution

Degradation

Figure 3. Sample before degradation (a) TEM image and (b) SEM image. Sample PBS degradation (c) TEM image and (d) SEM image. (e) TEM image of the sample in water degradation. (f) Comparison of the particle size of the different samples

Figure 4. Size distribution of each sample (a) before degradation, (b) PBS degradation, (c) water degradation

The best of the degradation: Increase the porosity

Table 1. BET area for each sample

	BET Area / m^2/g
Before Degradation	1132.4
PBS Degradation	707.5
Water Degradation	1111.1

Figure 5. (a) Nitrogen adsorption-desorption isotherms and (b) Porous size distribution of each sample

Conclusion

- Varying the aging time: obtain particles with a controllable size (100-200 nm).
- Modulate the particle surface: change the roughness of the surface.
- Degradation: increase the porosity of the mesoporous particles using different medium.
- The particles can be used in catalysis or biomedical applications due to their small size.

[1] Nanoparticulated silicas with bimodal porosity: chemical control of the pore sizes. J. El Haskouri et al., Inorg. Chem., 2008, 47, 8267; doi.org/10.1021/ic800893a
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SIZE, ROUGHNESS AND POROSITY CONTROL IN MESOPOROUS STÖBER-TYPE PARTICLES

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Mesoporous silica particles are the inorganic bedrock on which, through functionalization processes, it is possible to build up inorganic and hybrid nanomaterials with multiple emerging applications. In fact, they have been designed very complex systems involving sophisticated functionalities, although the role played by the inorganic silica support is frequently underestimated. Here, we report on mesoporous spherical silica particles synthesized by combining the atrane route (which starts from complexes including triethanolamine-related ligands as Si source) [1] and the Stöber method (which implies using hydro-alcoholic reaction media) [2]. A fine-tuning of the aging time (from minutes to 1 day) allows a kinetic control of the particle size (in the ca. 100-200 nm range) together with a remarkable particle-size homogeneity (Figure 1a). On the other hand, the particle-size dispersion is even reduced when the particles are aged under hydrothermal conditions, process that in turns results in a regular surface roughness (Figure 1b). Also, post-treatments at fixed pH values and using different media (water, PBS…) can induce a massive and controlled degradation, without size reduction, that generates a meso/macroporosity additional to that typical of the original material (associated to the templating effect of the micelles) (Figure 1c). The resulting Stöber-type particles show an enhanced porosity able to accommodate relatively large guest species.

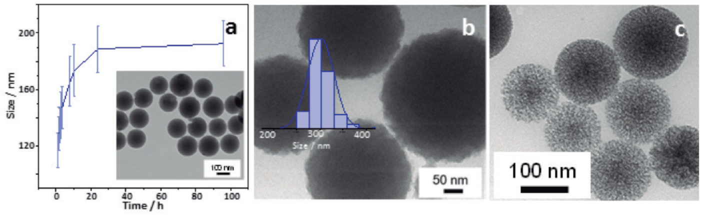

Figure 1: (a) Size vs time. TEM of the hydrothermal treated (b) and degraded (c) samples.

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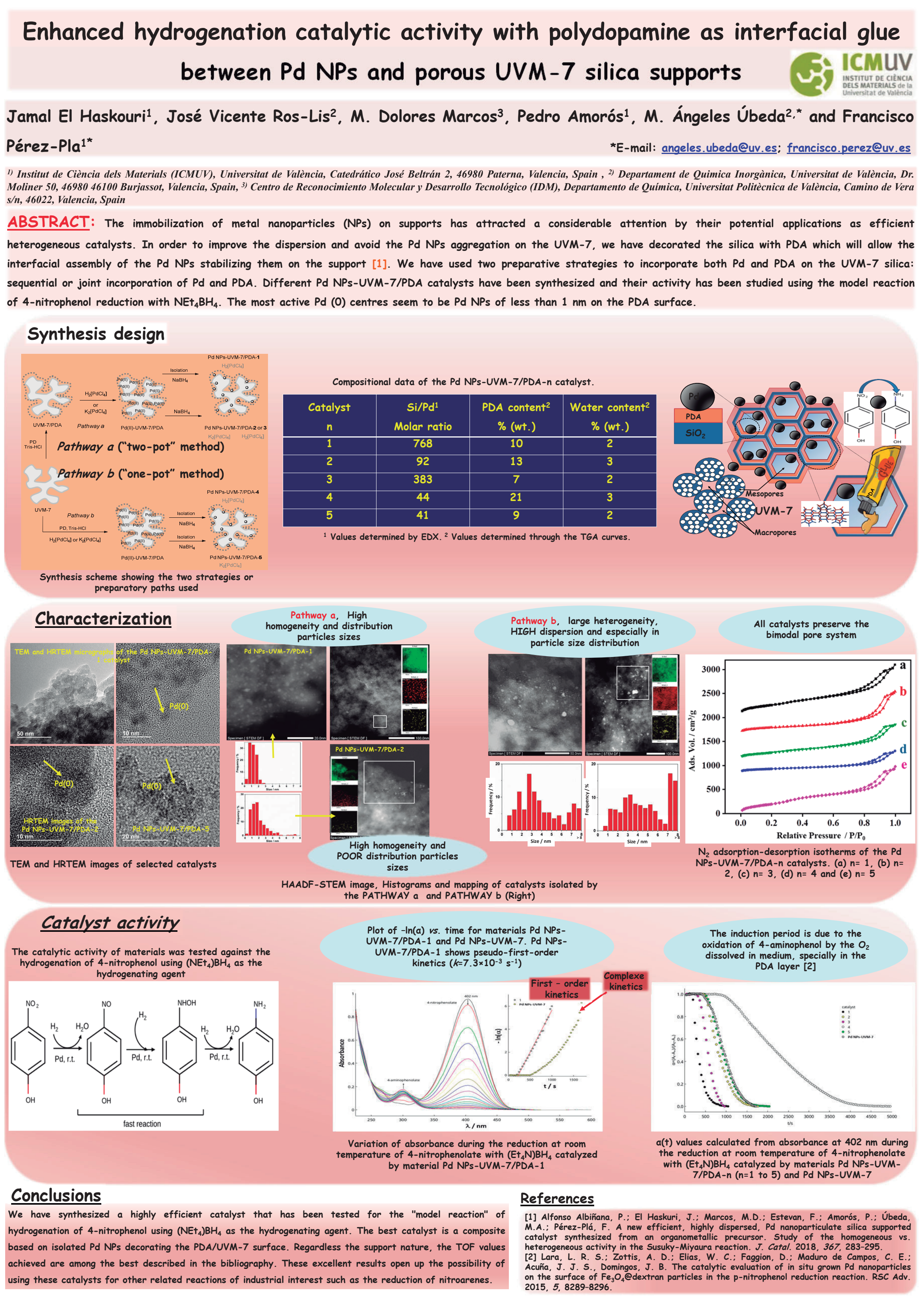

Enhanced hydrogenation catalytic activity with polydopamine as interfacial glue between Pd NPs and porous UVM-7 silica supports

Jamal El Haskouri[1], José Vicente Ros-Lis[2], M. Dolores Marcos[3], Pedro Amorós[1], M. Ángeles Úbeda[2,*] and Francisco Pérez-Pla[1*]

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ABSTRACT: The immobilization of metal nanoparticles (NPs) on supports has attracted a considerable attention by their potential applications as efficient heterogeneous catalysts. In order to improve the dispersion and avoid the Pd NPs aggregation on the UVM-7, we have decorated the silica with PDA which will allow the interfacial assembly of the Pd NPs stabilizing them on the support [1]. We have used two preparative strategies to incorporate both Pd and PDA on the UVM-7 silica: sequential or joint incorporation of Pd and PDA. Different Pd NPs-UVM-7/PDA catalysts have been synthesized and their activity has been studied using the model reaction of 4-nitrophenol reduction with NEt_4BH_4. The most active Pd (0) centres seem to be Pd NPs of less than 1 nm on the PDA surface.

Synthesis design

Synthesis scheme showing the two strategies or preparatory paths used

Compositional data of the Pd NPs-UVM-7/PDA-n catalyst.

Catalyst n	Si/Pd[1] Molar ratio	PDA content[2] % (wt.)	Water content[2] % (wt.)
1	768	10	2
2	92	13	3
3	383	7	2
4	44	21	3
5	41	9	2

[1] Values determined by EDX. [2] Values determined through the TGA curves.

Characterization

Pathway a, High homogeneity and distribution particles sizes

Pathway b, large heterogeneity, HIGH dispersion and especially in particle size distribution

All catalysts preserve the bimodal pore system

TEM and HRTEM micrographs of the Pd NPs-UVM-7/PDA-1 catalyst

HRTEM images of the Pd NPs-UVM-7/PDA-2

Pd NPs-UVM-7/PDA-5

TEM and HRTEM images of selected catalysts

Pd NPs-UVM-7/PDA-1

Pd NPs-UVM-7/PDA-2

High homogeneity and POOR distribution particles sizes

HAADF-STEM image, Histograms and mapping of catalysts isolated by the PATHWAY a and PATHWAY b (Right)

N_2 adsorption-desorption isotherms of the Pd NPs-UVM-7/PDA-n catalysts. (a) n= 1, (b) n= 2, (c) n= 3, (d) n= 4 and (e) n= 5

Catalyst activity

The catalytic activity of materials was tested against the hydrogenation of 4-nitrophenol using $(NEt_4)BH_4$ as the hydrogenating agent

Plot of −ln(a) *vs.* time for materials Pd NPs-UVM-7/PDA-1 and Pd NPs-UVM-7. Pd NPs-UVM-7/PDA-1 shows pseudo-first-order kinetics ($k=7.3\times10^{-3}$ s^{-1})

The induction period is due to the oxidation of 4-aminophenol by the O_2 dissolved in medium, specially in the PDA layer [2]

Variation of absorbance during the reduction at room temperature of 4-nitrophenolate with $(Et_4N)BH_4$ catalyzed by material Pd NPs-UVM-7/PDA-1

a(t) values calculated from absorbance at 402 nm during the reduction at room temperature of 4-nitrophenolate with $(Et_4N)BH_4$ catalyzed by materials Pd NPs-UVM-7/PDA-n (n=1 to 5) and Pd NPs-UVM-7

Conclusions

We have synthesized a highly efficient catalyst that has been tested for the "model reaction" of hydrogenation of 4-nitrophenol using $(NEt_4)BH_4$ as the hydrogenating agent. The best catalyst is a composite based on isolated Pd NPs decorating the PDA/UVM-7 surface. Regardless the support nature, the TOF values achieved are among the best described in the bibliography. These excellent results open up the possibility of using these catalysts for other related reactions of industrial interest such as the reduction of nitroarenes.

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ENHANCED HYDROGENATION CATALYTIC ACTIVITY WITH POLYDOPAMINE AS INTERFACIAL GLUE BETWEEN PD NPS AND POROUS UVM-7 SILICA SUPPORTS

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The immobilization of metal nanoparticles (NPs) on supports has attracted a considerable attention by their potential applications as efficient heterogeneous catalysts. Inspired by the adhesive proteins in mussels, we used PDA as interfacial glue that provides strong adhesion by intensive covalent and noncovalent bindings. In order to improve the dispersion and avoid the Pd NPs aggregation on the UVM-7, we have decorated the silica with PDA which will allow the interfacial assembly of the Pd NPs stabilizing them on the support [1]. We have used two preparative strategies to incorporate both Pd and PDA on the UVM-7 silica: sequential or joint incorporation of Pd and PDA. The best catalysts were synthesized through a "two pot" methodology in which in a first step the silica surface is covered with PDA. During the second step the incorporation of Pd(II) is carried out by using $H_2[PdCl_4]$ or $K_2[PdCl_4]$ complexes as metal source followed by the reduction with $NaBH_4$ to favour the Pd(0) particle formation (Figure 1a and b). Different Pd NPs-UVM-7/PDA catalysts have been synthesized and their activity has been studied using the model reaction of 4-nitrophenol reduction with NEt_4BH_4 (Figure 1c). The most active Pd (0) centres seem to be Pd NPs of less than 1 nm on the PDA surface. The efficiency of the catalysts obtained is superior to that of similar materials without PDA. The TOF values achieved are among the best described in the literature: $TOF_{1/2}/h^{-1}$= 8470.

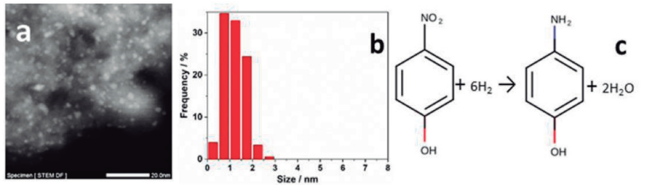

Figure 1: (a) HAADF-STEM image. (b) NP size distribution. (c) Model reaction used.

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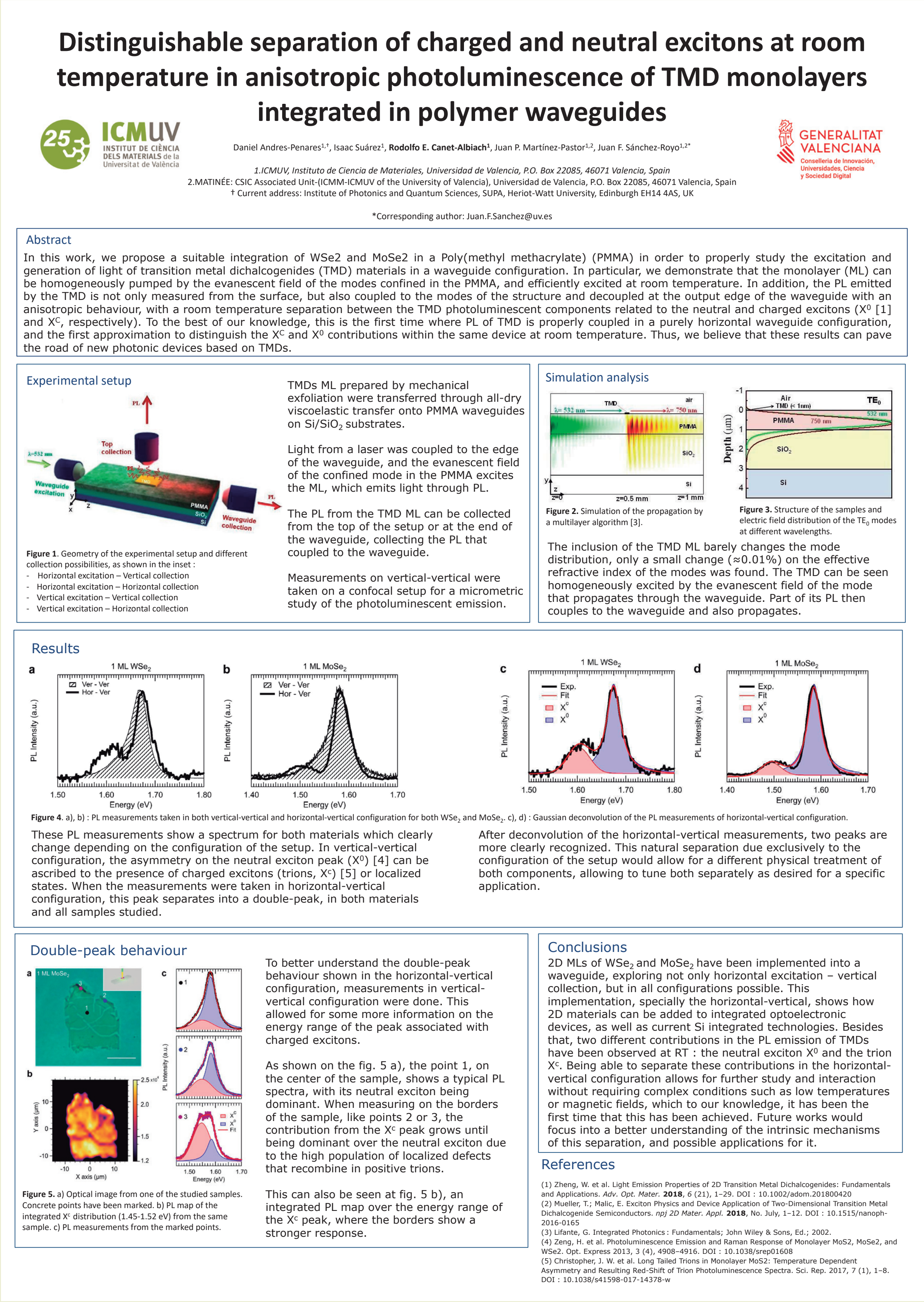

Distinguishable separation of charged and neutral excitons at room temperature in anisotropic photoluminescence of TMD monolayers integrated in polymer waveguides

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Abstract

In this work, we propose a suitable integration of WSe2 and MoSe2 in a Poly(methyl methacrylate) (PMMA) in order to properly study the excitation and generation of light of transition metal dichalcogenides (TMD) materials in a waveguide configuration. In particular, we demonstrate that the monolayer (ML) can be homogeneously pumped by the evanescent field of the modes confined in the PMMA, and efficiently excited at room temperature. In addition, the PL emitted by the TMD is not only measured from the surface, but also coupled to the modes of the structure and decoupled at the output edge of the waveguide with an anisotropic behaviour, with a room temperature separation between the TMD photoluminescent components related to the neutral and charged excitons (X^0 [1] and X^C, respectively). To the best of our knowledge, this is the first time where PL of TMD is properly coupled in a purely horizontal waveguide configuration, and the first approximation to distinguish the X^C and X^0 contributions within the same device at room temperature. Thus, we believe that these results can pave the road of new photonic devices based on TMDs.

Experimental setup

Figure 1. Geometry of the experimental setup and different collection possibilities, as shown in the inset :
- Horizontal excitation – Vertical collection
- Horizontal excitation – Horizontal collection
- Vertical excitation – Vertical collection
- Vertical excitation – Horizontal collection

TMDs ML prepared by mechanical exfoliation were transferred through all-dry viscoelastic transfer onto PMMA waveguides on Si/SiO_2 substrates.

Light from a laser was coupled to the edge of the waveguide, and the evanescent field of the confined mode in the PMMA excites the ML, which emits light through PL.

The PL from the TMD ML can be collected from the top of the setup or at the end of the waveguide, collecting the PL that coupled to the waveguide.

Measurements on vertical-vertical were taken on a confocal setup for a micrometric study of the photoluminescent emission.

Simulation analysis

Figure 2. Simulation of the propagation by a multilayer algorithm [3].

Figure 3. Structure of the samples and electric field distribution of the TE_0 modes at different wavelengths.

The inclusion of the TMD ML barely changes the mode distribution, only a small change (≈0.01%) on the effective refractive index of the modes was found. The TMD can be seen homogeneously excited by the evanescent field of the mode that propagates through the waveguide. Part of its PL then couples to the waveguide and also propagates.

Results

Figure 4. a), b) : PL measurements taken in both vertical-vertical and horizontal-vertical configuration for both WSe_2 and $MoSe_2$. c), d) : Gaussian deconvolution of the PL measurements of horizontal-vertical configuration.

These PL measurements show a spectrum for both materials which clearly change depending on the configuration of the setup. In vertical-vertical configuration, the asymmetry on the neutral exciton peak (X^0) [4] can be ascribed to the presence of charged excitons (trions, X^c) [5] or localized states. When the measurements were taken in horizontal-vertical configuration, this peak separates into a double-peak, in both materials and all samples studied.

After deconvolution of the horizontal-vertical measurements, two peaks are more clearly recognized. This natural separation due exclusively to the configuration of the setup would allow for a different physical treatment of both components, allowing to tune both separately as desired for a specific application.

Double-peak behaviour

Figure 5. a) Optical image from one of the studied samples. Concrete points have been marked. b) PL map of the integrated X^c distribution (1.45-1.52 eV) from the same sample. c) PL measurements from the marked points.

To better understand the double-peak behaviour shown in the horizontal-vertical configuration, measurements in vertical-vertical configuration were done. This allowed for some more information on the energy range of the peak associated with charged excitons.

As shown on the fig. 5 a), the point 1, on the center of the sample, shows a typical PL spectra, with its neutral exciton being dominant. When measuring on the borders of the sample, like points 2 or 3, the contribution from the X^c peak grows until being dominant over the neutral exciton due to the high population of localized defects that recombine in positive trions.

This can also be seen at fig. 5 b), an integrated PL map over the energy range of the X^c peak, where the borders show a stronger response.

Conclusions

2D MLs of WSe_2 and $MoSe_2$ have been implemented into a waveguide, exploring not only horizontal excitation – vertical collection, but in all configurations possible. This implementation, specially the horizontal-vertical, shows how 2D materials can be added to integrated optoelectronic devices, as well as current Si integrated technologies. Besides that, two different contributions in the PL emission of TMDs have been observed at RT : the neutral exciton X^0 and the trion X^c. Being able to separate these contributions in the horizontal-vertical configuration allows for further study and interaction without requiring complex conditions such as low temperatures or magnetic fields, which to our knowledge, it has been the first time that this has been achieved. Future works would focus into a better understanding of the intrinsic mechanisms of this separation, and possible applications for it.

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DISTINGUISHABLE SEPARATION OF CHARGED AND NEUTRAL EXCITONS AT ROOM TEMPERATURE IN ANISOTROPIC PHOTOLUMINESCENCE OF TMD MONOLAYERS INTEGRATED IN POLYMER WAVEGUIDES

Daniel Andres-Penares[1,†], Isaac Suárez[1], Rodolfo E. Canet-Albiach[1], Juan P. Martínez-Pastor[1,2], Juan F. Sánchez-Royo[1,2*]

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The photoluminescence (PL) emission properties of atomically thin layers of transition metal dichalcogenides (TMDs) have been extensively studied [1, 2], due to its high intensity and efficiency, even at room temperature. These properties make them exciting candidates to be integrated into photonic circuits. For this reason, we have proposed in this work the integration of WSe2 and MoSe2 monolayers in a Polymethylmetacrylate (PMMA) waveguide in order to study how the excitation and generation of light in TMD materials works in a waveguide configuration. Particularly, we show how the ML can be excited through the waveguide, using the evanescent fields of the modes confined in the PMMA, excited from the edge of the waveguide. Also, it is demonstrated that the PL emitted by the TMD can be measured from the surface and through the waveguide, due to the coupling of the PL with the modes of the structure, decoupling at the opposite edge from the excitation. Besides, it is shown how the PL spectra shows an anisotropic behaviour that can be studied thanks to the different collection configurations of the experimental setup as shown in figure 1.

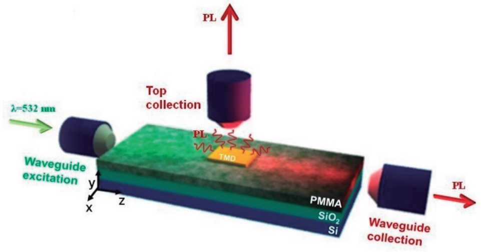

Figure 1. Geometry of the experimental setup and different collection possibilities.

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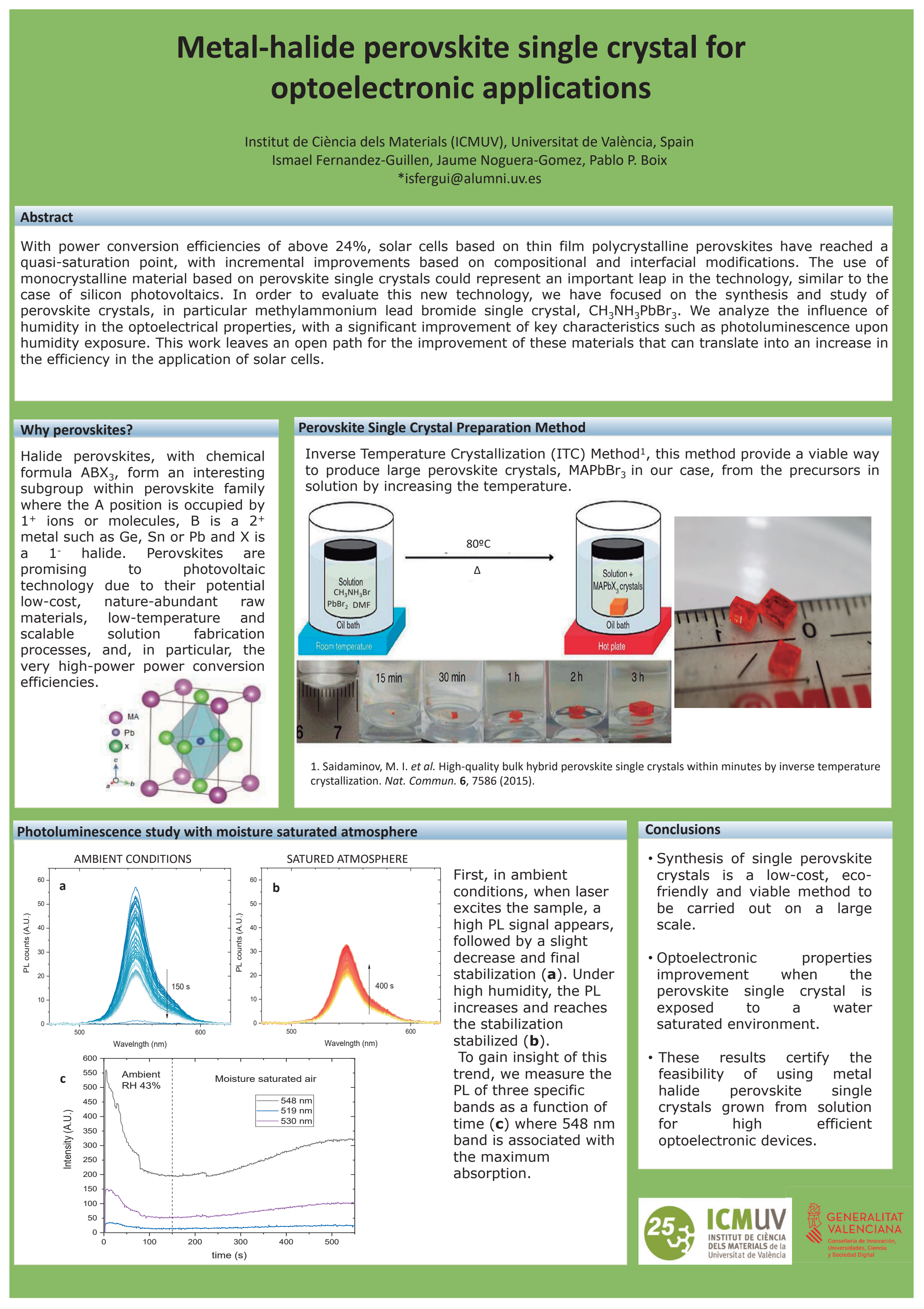

Metal-halide perovskite single crystal for optoelectronic applications

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Abstract

With power conversion efficiencies of above 24%, solar cells based on thin film polycrystalline perovskites have reached a quasi-saturation point, with incremental improvements based on compositional and interfacial modifications. The use of monocrystalline material based on perovskite single crystals could represent an important leap in the technology, similar to the case of silicon photovoltaics. In order to evaluate this new technology, we have focused on the synthesis and study of perovskite crystals, in particular methylammonium lead bromide single crystal, $CH_3NH_3PbBr_3$. We analyze the influence of humidity in the optoelectrical properties, with a significant improvement of key characteristics such as photoluminescence upon humidity exposure. This work leaves an open path for the improvement of these materials that can translate into an increase in the efficiency in the application of solar cells.

Why perovskites?

Halide perovskites, with chemical formula ABX_3, form an interesting subgroup within perovskite family where the A position is occupied by 1^+ ions or molecules, B is a 2^+ metal such as Ge, Sn or Pb and X is a 1^- halide. Perovskites are promising to photovoltaic technology due to their potential low-cost, nature-abundant raw materials, low-temperature and scalable solution fabrication processes, and, in particular, the very high-power power conversion efficiencies.

Perovskite Single Crystal Preparation Method

Inverse Temperature Crystallization (ITC) Method[1], this method provide a viable way to produce large perovskite crystals, $MAPbBr_3$ in our case, from the precursors in solution by increasing the temperature.

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Photoluminescence study with moisture saturated atmosphere

First, in ambient conditions, when laser excites the sample, a high PL signal appears, followed by a slight decrease and final stabilization (**a**). Under high humidity, the PL increases and reaches the stabilization stabilized (**b**).

To gain insight of this trend, we measure the PL of three specific bands as a function of time (**c**) where 548 nm band is associated with the maximum absorption.

Conclusions

- Synthesis of single perovskite crystals is a low-cost, eco-friendly and viable method to be carried out on a large scale.
- Optoelectronic properties improvement when the perovskite single crystal is exposed to a water saturated environment.
- These results certify the feasibility of using metal halide perovskite single crystals grown from solution for high efficient optoelectronic devices.

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METAL-HALIDE PEROVSKITE SINGLE CRYSTAL FOR OPTOELECTRONIC APPLICATIONS

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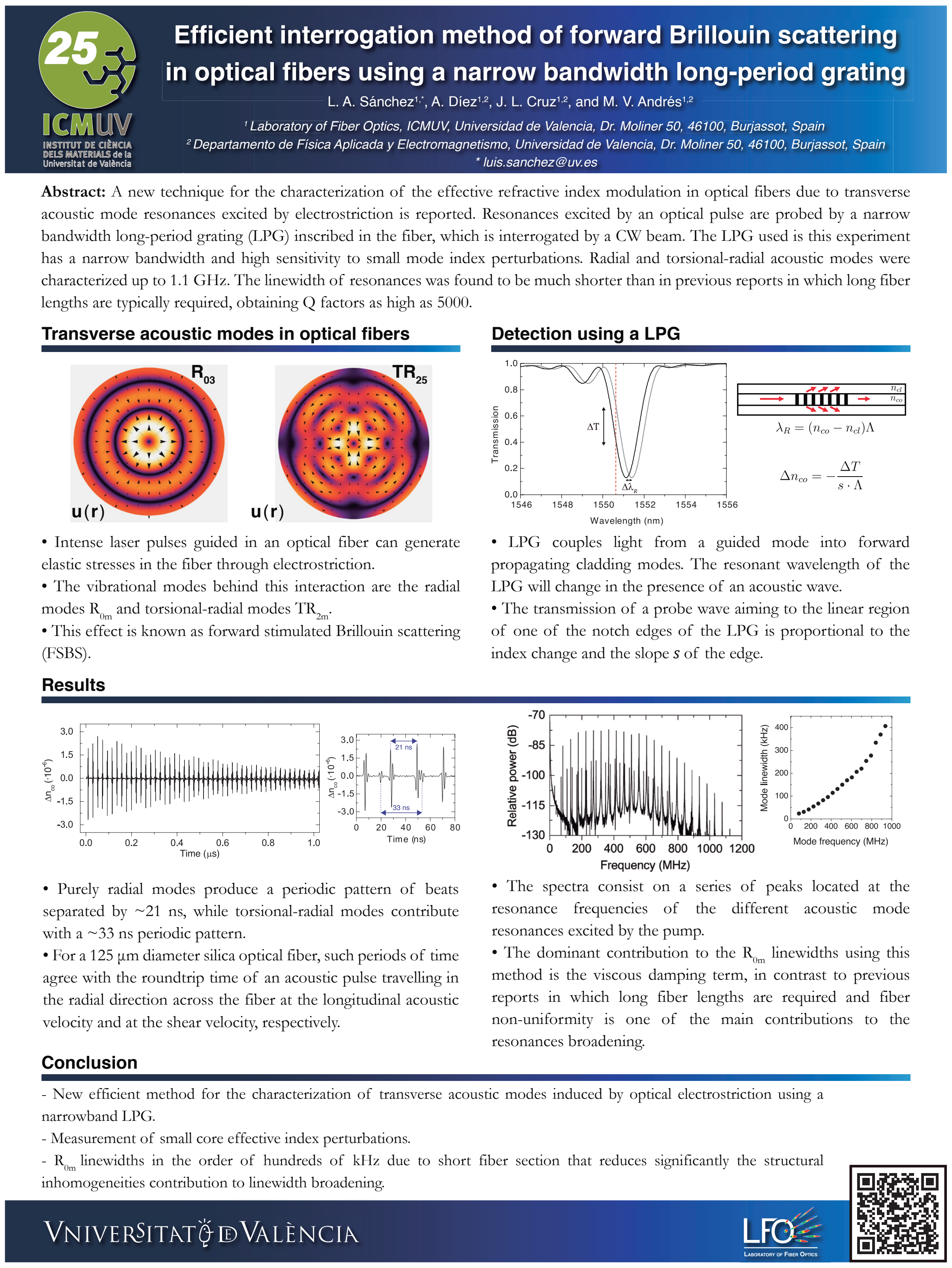
The unprecedented evolution of metal halide perovskites photovoltaics was the key motivation to explore the outstanding optoelectronic properties of this family of materials. Currently, with power conversion efficiencies of above 24%, solar cells based on thin film polycrystalline perovskites have reached a quasi-saturation point, with incremental improvements based on compositional, interfacial modifications. The use of monocrystalline material based on perovskite single crystals could represent an important leap in the technology, similar to the case of silicon photovoltaics. In

order to evaluate this new technology, we have focused on the synthesis and study of perovskite crystals, exploring how different synthesis conditions can vary the optoelectronic properties. We analyze the influence of humidity in the optoelectrical properties, with a significant improvement of

key characteristics such photoluminescence upon humidity exposure. This work leaves an open path for the improvement of these materials that can translate into an increase in the efficiency in the application of solar cells.



Efficient interrogation method of forward Brillouin scattering in optical fibers using a narrow bandwidth long-period grating

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Abstract: A new technique for the characterization of the effective refractive index modulation in optical fibers due to transverse acoustic mode resonances excited by electrostriction is reported. Resonances excited by an optical pulse are probed by a narrow bandwidth long-period grating (LPG) inscribed in the fiber, which is interrogated by a CW beam. The LPG used is this experiment has a narrow bandwidth and high sensitivity to small mode index perturbations. Radial and torsional-radial acoustic modes were characterized up to 1.1 GHz. The linewidth of resonances was found to be much shorter than in previous reports in which long fiber lengths are typically required, obtaining Q factors as high as 5000.

Transverse acoustic modes in optical fibers

- Intense laser pulses guided in an optical fiber can generate elastic stresses in the fiber through electrostriction.
- The vibrational modes behind this interaction are the radial modes R_{0m} and torsional-radial modes TR_{2m}.
- This effect is known as forward stimulated Brillouin scattering (FSBS).

Detection using a LPG

$$\lambda_R = (n_{co} - n_{cl})\Lambda$$

$$\Delta n_{co} = -\frac{\Delta T}{s \cdot \Lambda}$$

- LPG couples light from a guided mode into forward propagating cladding modes. The resonant wavelength of the LPG will change in the presence of an acoustic wave.
- The transmission of a probe wave aiming to the linear region of one of the notch edges of the LPG is proportional to the index change and the slope *s* of the edge.

Results

- Purely radial modes produce a periodic pattern of beats separated by ~21 ns, while torsional-radial modes contribute with a ~33 ns periodic pattern.
- For a 125 μm diameter silica optical fiber, such periods of time agree with the roundtrip time of an acoustic pulse travelling in the radial direction across the fiber at the longitudinal acoustic velocity and at the shear velocity, respectively.

- The spectra consist on a series of peaks located at the resonance frequencies of the different acoustic mode resonances excited by the pump.
- The dominant contribution to the R_{0m} linewidths using this method is the viscous damping term, in contrast to previous reports in which long fiber lengths are required and fiber non-uniformity is one of the main contributions to the resonances broadening.

Conclusion

- New efficient method for the characterization of transverse acoustic modes induced by optical electrostriction using a narrowband LPG.
- Measurement of small core effective index perturbations.
- R_{0m} linewidths in the order of hundreds of kHz due to short fiber section that reduces significantly the structural inhomogeneities contribution to linewidth broadening.

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EFFICIENT INTERROGATION METHOD OF FORWARD BRILLOUIN SCATTERING IN OPTICAL FIBERS USING A NARROW BANDWIDTH LONG-PERIOD GRATING

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Transverse acoustic waves in optical fibers are excited by electrostriction when a high power optical pulse propagates in the fiber. This effect is known as forward stimulated Brillouin scattering (FSBS). The acoustic vibrational modes behind this interaction are the radial modes R_{0m} and torsional-radial modes TR_{2m} [1]. Typically, the detection techniques of these modes are mostly based on the direct analysis of the light scattered by the acoustic waves using interferometric techniques [2]. Here we propose an alternative method employing a long-period fiber grating (LPG) which is used to translate effective index modulation into amplitude modulation of a probe beam. LPGs are fiber devices that couple energy from the fundamental optical core mode to co-propagating cladding modes. The resonance wavelength of the grating depends on the difference between the effective index of the coupled modes. The perturbation in the effective index of the core optical mode as a result of the acoustic wave causes the shift of the notch, thus modifying the transmission of the probe laser (Figure 1). The short fiber section required by this method reduces significantly the structural inhomogeneities contribution to the linewidth broadening of the acoustic modes and allows to detect effective index changes down to 10^{-9}.

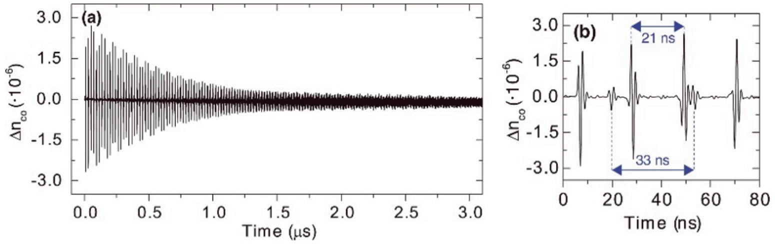

Figure 1: (a) Core effective index variation of the LPG for a pump peak power of 7.4 kW. (b) Detailed plot of the first 80 ns with visible excitation of R_{0m} and TR_{2m} modes.

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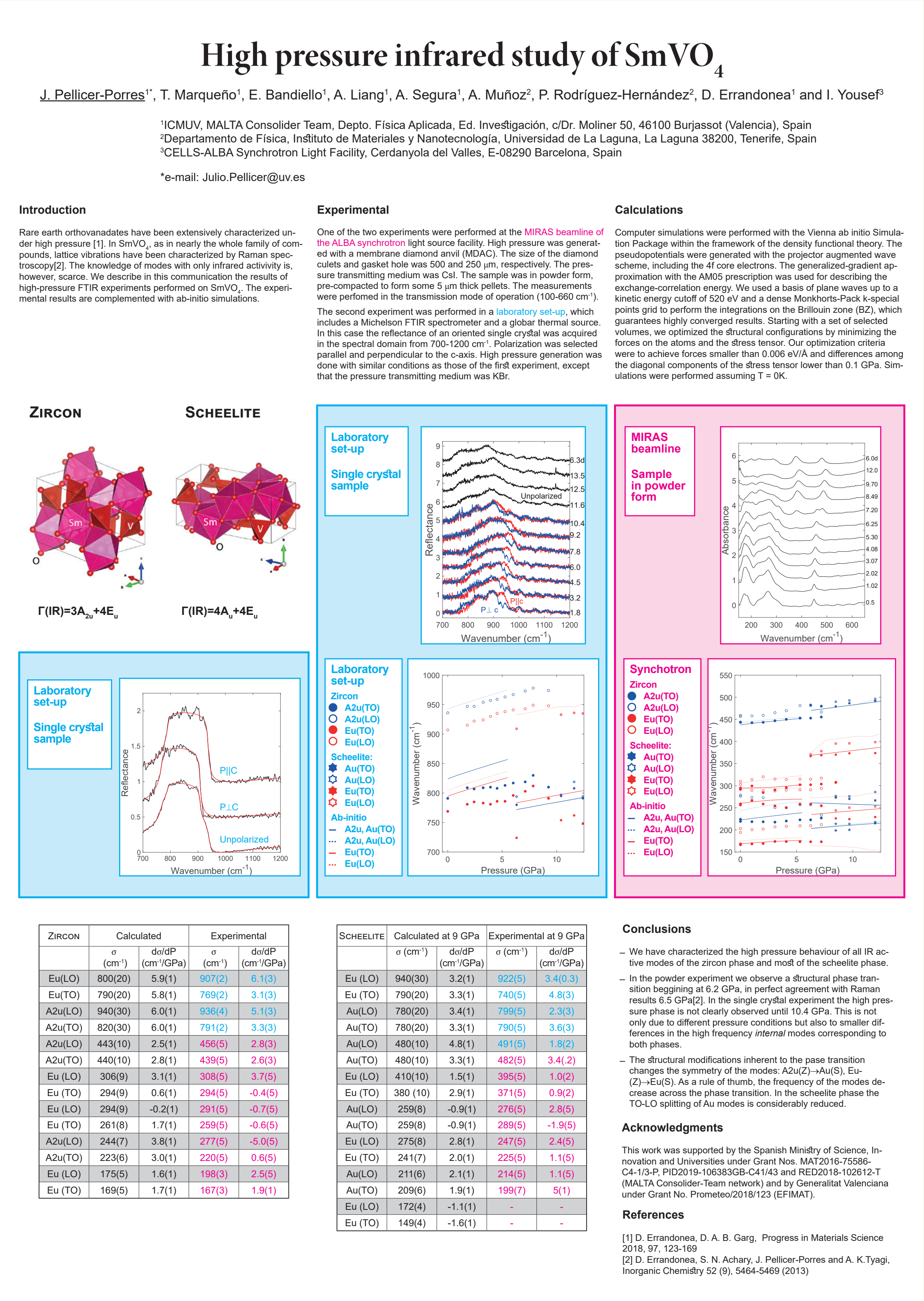

High pressure infrared study of SmVO$_4$

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Introduction

Rare earth orthovanadates have been extensively characterized under high pressure [1]. In SmVO$_4$, as in nearly the whole family of compounds, lattice vibrations have been characterized by Raman spectroscopy[2]. The knowledge of modes with only infrared activity is, however, scarce. We describe in this communication the results of high-pressure FTIR experiments performed on SmVO$_4$. The experimental results are complemented with ab-initio simulations.

Experimental

One of the two experiments were performed at the MIRAS beamline of the ALBA synchrotron light source facility. High pressure was generated with a membrane diamond anvil (MDAC). The size of the diamond culets and gasket hole was 500 and 250 μm, respectively. The pressure transmitting medium was CsI. The sample was in powder form, pre-compacted to form some 5 μm thick pellets. The measurements were perfomed in the transmission mode of operation (100-660 cm^{-1}).

The second experiment was performed in a laboratory set-up, which includes a Michelson FTIR spectrometer and a globar thermal source. In this case the reflectance of an oriented single crystal was acquired in the spectral domain from 700-1200 cm^{-1}. Polarization was selected parallel and perpendicular to the c-axis. High pressure generation was done with similar conditions as those of the first experiment, except that the pressure transmitting medium was KBr.

Calculations

Computer simulations were performed with the Vienna ab initio Simulation Package within the framework of the density functional theory. The pseudopotentials were generated with the projector augmented wave scheme, including the 4f core electrons. The generalized-gradient approximation with the AM05 prescription was used for describing the exchange-correlation energy. We used a basis of plane waves up to a kinetic energy cutoff of 520 eV and a dense Monkhorts-Pack k-special points grid to perform the integrations on the Brillouin zone (BZ), which guarantees highly converged results. Starting with a set of selected volumes, we optimized the structural configurations by minimizing the forces on the atoms and the stress tensor. Our optimization criteria were to achieve forces smaller than 0.006 eV/Å and differences among the diagonal components of the stress tensor lower than 0.1 GPa. Simulations were performed assuming T = 0K.

ZIRCON

$\Gamma(IR)=3A_{2u}+4E_u$

SCHEELITE

$\Gamma(IR)=4A_u+4E_u$

ZIRCON	Calculated		Experimental	
	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)
Eu(LO)	800(20)	5.9(1)	907(2)	6.1(3)
Eu(TO)	790(20)	5.8(1)	769(2)	3.1(3)
A2u(LO)	940(30)	6.0(1)	936(4)	5.1(3)
A2u(TO)	820(30)	6.0(1)	791(2)	3.3(3)
A2u(LO)	443(10)	2.5(1)	456(5)	2.8(3)
A2u(TO)	440(10)	2.8(1)	439(5)	2.6(3)
Eu (LO)	306(9)	3.1(1)	308(5)	3.7(5)
Eu (TO)	294(9)	0.6(1)	294(5)	-0.4(5)
Eu (LO)	294(9)	-0.2(1)	291(5)	-0.7(5)
Eu (TO)	261(8)	1.7(1)	259(5)	-0.6(5)
A2u(LO)	244(7)	3.8(1)	277(5)	-5.0(5)
A2u(TO)	223(6)	3.0(1)	220(5)	0.6(5)
Eu (LO)	175(5)	1.6(1)	198(3)	2.5(5)
Eu (TO)	169(5)	1.7(1)	167(3)	1.9(1)

SCHEELITE	Calculated at 9 GPa		Experimental at 9 GPa	
	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)	σ (cm^{-1})	dσ/dP (cm^{-1}/GPa)
Eu (LO)	940(30)	3.2(1)	922(5)	3.4(0.3)
Eu (TO)	790(20)	3.3(1)	740(5)	4.8(3)
Au(LO)	780(20)	3.4(1)	799(5)	2.3(3)
Au(TO)	780(20)	3.3(1)	790(5)	3.6(3)
Au(LO)	480(10)	4.8(1)	491(5)	1.8(2)
Au(TO)	480(10)	3.3(1)	482(5)	3.4(.2)
Eu (LO)	410(10)	1.5(1)	395(5)	1.0(2)
Eu (TO)	380 (10)	2.9(1)	371(5)	0.9(2)
Au(LO)	259(8)	-0.9(1)	276(5)	2.8(5)
Au(TO)	259(8)	-0.9(1)	289(5)	-1.9(5)
Eu (LO)	275(8)	2.8(1)	247(5)	2.4(5)
Eu (TO)	241(7)	2.0(1)	225(5)	1.1(5)
Au(LO)	211(6)	2.1(1)	214(5)	1.1(5)
Au(TO)	209(6)	1.9(1)	199(7)	5(1)
Eu (LO)	172(4)	-1.1(1)	-	-
Eu (TO)	149(4)	-1.6(1)	-	-

Conclusions

- We have characterized the high pressure behaviour of all IR active modes of the zircon phase and most of the scheelite phase.
- In the powder experiment we observe a structural phase transition beggining at 6.2 GPa, in perfect agreement with Raman results 6.5 GPa[2]. In the single crystal experiment the high pressure phase is not clearly observed until 10.4 GPa. This is not only due to different pressure conditions but also to smaller differences in the high frequency *internal* modes corresponding to both phases.
- The structural modifications inherent to the pase transition changes the symmetry of the modes: A2u(Z)→Au(S), Eu-(Z)→Eu(S). As a rule of thumb, the frequency of the modes decrease across the phase transition. In the scheelite phase the TO-LO splitting of Au modes is considerably reduced.

Acknowledgments

This work was supported by the Spanish Ministry of Science, Innovation and Universities under Grant Nos. MAT2016-75586-C4-1/3-P, PID2019-106383GB-C41/43 and RED2018-102612-T (MALTA Consolider-Team network) and by Generalitat Valenciana under Grant No. Prometeo/2018/123 (EFIMAT).

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HIGH PRESSURE INFRARED STUDY OF SmVO$_4$

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Rare earth orthovanadates have been extensively characterized under high pressure [1]. In nearly all compounds lattice vibrations have been characterized by Raman spectroscopy. The knowledge of modes with only infrared activity is, however, scarce. We will describe in this communication the results of high-pressure FTIR experiments performed on SmVO4. The experimental results are complemented with ab-initio simulations.

Computer simulations were performed with the Vienna ab initio Simulation Package within the framework of the density functional theory. We carried out two experiments. In both of them high pressure was generated with a membrane diamond anvil (MDAC). The first one was performed at the MIRAS beamline of the ALBA synchrotron light source facility. The sample was in powder form. The measurements were perfomed in the transmission mode of operation (100-660 cm-1). The second experiment was performed in a laboratory set-up, which includes a Michelson FTIR spectrometer and a globar thermal source. In this case the reflectance of an oriented single crystal was acquired in the spectral domain from 700-1200 cm-1. Polarization was selected parallel and perpendicular to the c-axis.

We have characterized the high pressure behaviour of all IR active modes of the zircon phase and most of the scheelite phase. In the powder experiment we observe a structural phase transition beggining at 6.2 GPa, in perfect agreement with Raman results 6.5 GPa[2]. In the single crystal experiment the high pressure phase is not clearly observed until 10.4 GPa. This is not only due to different pressure conditions but also to smaller differences in the high frequency internal modes corresponding to both phases. The structural modifications inherent to the phase transition change the symmetry of the modes: A$_{2u}$(Z)→A$_u$(S), E$_u$(Z)→E$_u$(S). As a rule of thumb, the frequency of the modes decrease across the phase transition. In the scheelite phase the TO-LO splitting of Au modes is considerably reduced.

1] D. Errandonea, D. A. B. Garg, Progress in Materials Science 2018, 97, 123-169.

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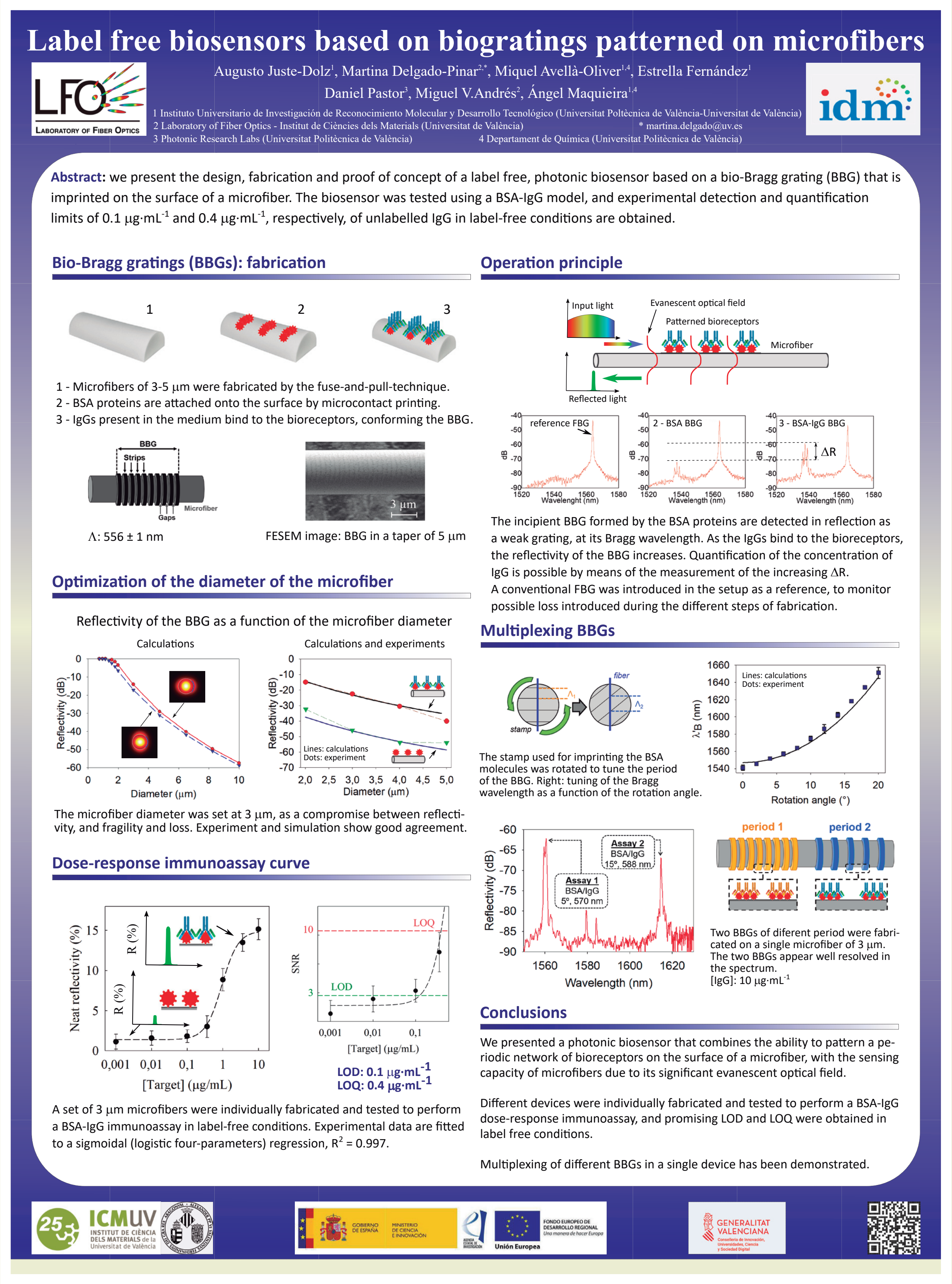

Label free biosensors based on biogratings patterned on microfibers

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Abstract: we present the design, fabrication and proof of concept of a label free, photonic biosensor based on a bio-Bragg grating (BBG) that is imprinted on the surface of a microfiber. The biosensor was tested using a BSA-IgG model, and experimental detection and quantification limits of 0.1 $\mu g\cdot mL^{-1}$ and 0.4 $\mu g\cdot mL^{-1}$, respectively, of unlabelled IgG in label-free conditions are obtained.

Bio-Bragg gratings (BBGs): fabrication

1 - Microfibers of 3-5 μm were fabricated by the fuse-and-pull-technique.
2 - BSA proteins are attached onto the surface by microcontact printing.
3 - IgGs present in the medium bind to the bioreceptors, conforming the BBG.

Λ: 556 ± 1 nm

FESEM image: BBG in a taper of 5 μm

Optimization of the diameter of the microfiber

Reflectivity of the BBG as a function of the microfiber diameter

The microfiber diameter was set at 3 μm, as a compromise between reflectivity, and fragility and loss. Experiment and simulation show good agreement.

Dose-response immunoassay curve

LOD: 0.1 $\mu g\cdot mL^{-1}$
LOQ: 0.4 $\mu g\cdot mL^{-1}$

A set of 3 μm microfibers were individually fabricated and tested to perform a BSA-IgG immunoassay in label-free conditions. Experimental data are fitted to a sigmoidal (logistic four-parameters) regression, $R^2 = 0.997$.

Operation principle

The incipient BBG formed by the BSA proteins are detected in reflection as a weak grating, at its Bragg wavelength. As the IgGs bind to the bioreceptors, the reflectivity of the BBG increases. Quantification of the concentration of IgG is possible by means of the measurement of the increasing ΔR.
A conventional FBG was introduced in the setup as a reference, to monitor possible loss introduced during the different steps of fabrication.

Multiplexing BBGs

The stamp used for imprinting the BSA molecules was rotated to tune the period of the BBG. Right: tuning of the Bragg wavelength as a function of the rotation angle.

Two BBGs of diferent period were fabricated on a single microfiber of 3 μm. The two BBGs appear well resolved in the spectrum.
[IgG]: 10 $\mu g\cdot mL^{-1}$

Conclusions

We presented a photonic biosensor that combines the ability to pattern a periodic network of bioreceptors on the surface of a microfiber, with the sensing capacity of microfibers due to its significant evanescent optical field.

Different devices were individually fabricated and tested to perform a BSA-IgG dose-response immunoassay, and promising LOD and LOQ were obtained in label free conditions.

Multiplexing of different BBGs in a single device has been demonstrated.

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LABEL FREE BIOSENSORS BASED ON BIOGRATINGS PATTERNED ON MICROFIBERS

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The development of photonic biosensors is currently a research topic of high interest, with a significant, potential impact on industry and medicine. In particular, label-free biosensors based on optical fibers or microfibers can lead to miniaturized, inexpensive and low-loss devices. Here, we present the design, fabrication, and proof of concept of a novel biosensor based on a bio-Bragg-grating (BBG) that is imprinted on the surface of a microfiber.

Our approach combines the ability to pattern a periodic network of bioreceptors on the surface of a microfiber (3 mm in diameter), with the sensing capacity of microfibers due to its significant evanescent optical field. The bioreceptors (BSA, in our case) are placed in a periodic fashion onto the fiber surface by microcontact printing [1], with a period of 556 ±1 nm. The interaction between the fundamental optical mode of the microfiber and this incipient BBG leads to a weak reflection peak in the optical response of the device, which is spectrally located at its Bragg wavelength, see Fig. 1 (a). The biosensing transduction principle relies on the fact that, if the specific target (IgGs in this case) is present in the external medium, it will bind to the bioreceptors that conform the BBG, increasing its modulation depth. As a result, it will be possible to quantify the concentration of specific IgGs by measuring the reflectivity of the BBG, see inset in Fig. 1 (b). A dosis-response curve of an experimental immunoassay is shown in Fig. 1 (b), fitted to a sigmoidal (logistic 4 parameters) regression. From these results, experimental detection and quantification limits of 0.1 $\mu g\ mL^{-1}$ and 0.4 $\mu g\ mL^{-1}$, respectively, of unlabelled IgG in label-free conditions are obtained.

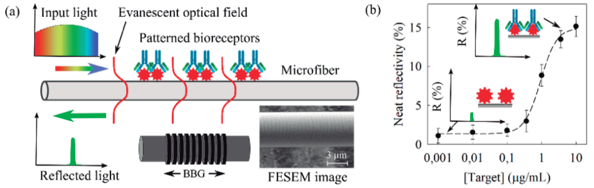

Figure 1 (a) Scheme of a BBG and FESEM image. (b) Experimental dose-response immunoassay curve.

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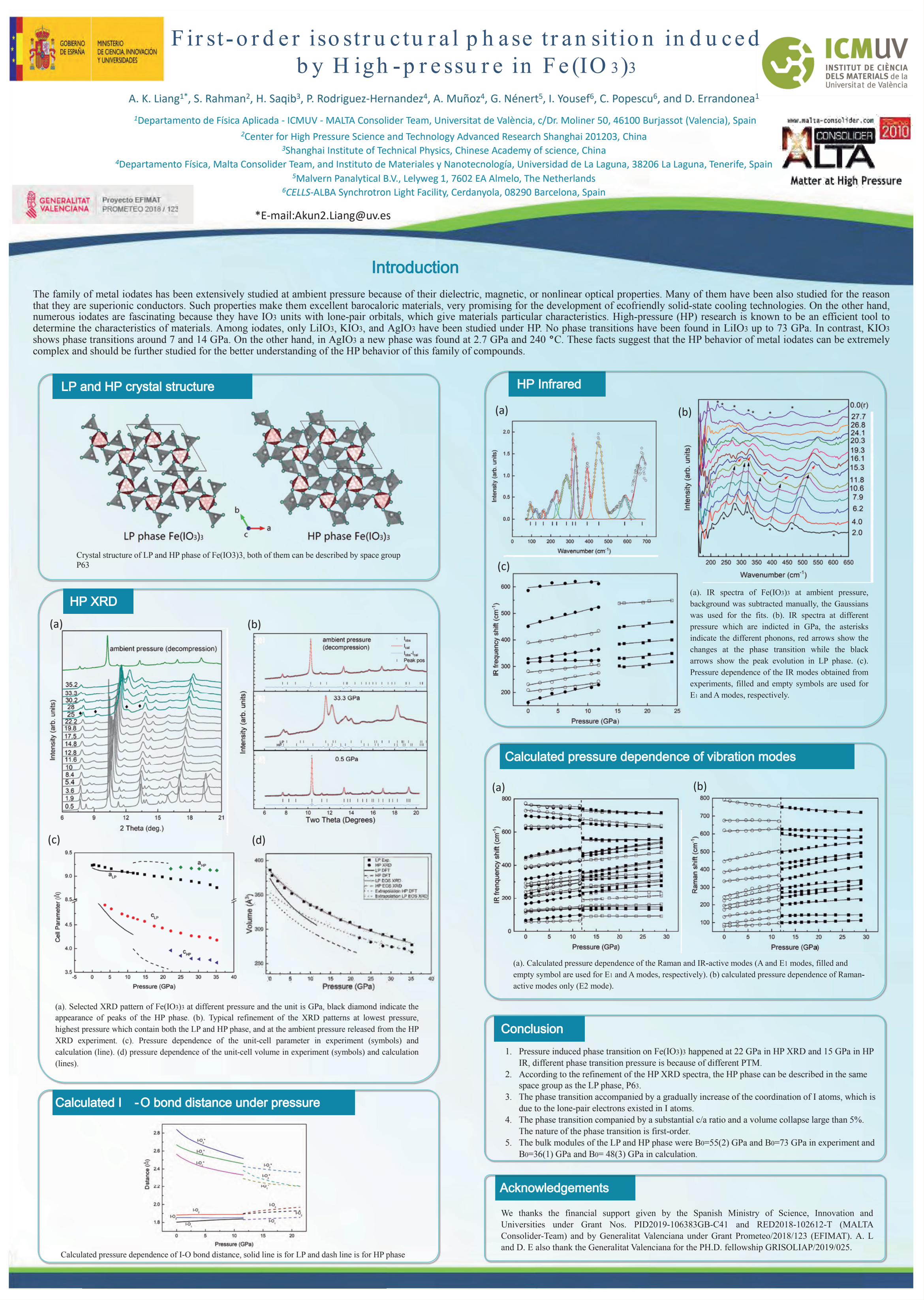

First-order isostructural phase transition induced by High-pressure in Fe(IO$_3$)$_3$

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Introduction

The family of metal iodates has been extensively studied at ambient pressure because of their dielectric, magnetic, or nonlinear optical properties. Many of them have been also studied for the reason that they are superionic conductors. Such properties make them excellent barocaloric materials, very promising for the development of ecofriendly solid-state cooling technologies. On the other hand, numerous iodates are fascinating because they have IO$_3$ units with lone-pair orbitals, which give materials particular characteristics. High-pressure (HP) research is known to be an efficient tool to determine the characteristics of materials. Among iodates, only LiIO$_3$, KIO$_3$, and AgIO$_3$ have been studied under HP. No phase transitions have been found in LiIO$_3$ up to 73 GPa. In contrast, KIO$_3$ shows phase transitions around 7 and 14 GPa. On the other hand, in AgIO$_3$ a new phase was found at 2.7 GPa and 240 °C. These facts suggest that the HP behavior of metal iodates can be extremely complex and should be further studied for the better understanding of the HP behavior of this family of compounds.

LP and HP crystal structure

LP phase Fe(IO$_3$)$_3$ HP phase Fe(IO$_3$)$_3$

Crystal structure of LP and HP phase of Fe(IO3)3, both of them can be described by space group P63

HP XRD

(a). Selected XRD pattern of Fe(IO$_3$)$_3$ at different pressure and the unit is GPa, black diamond indicate the appearance of peaks of the HP phase. (b). Typical refinement of the XRD patterns at lowest pressure, highest pressure which contain both the LP and HP phase, and at the ambient pressure released from the HP XRD experiment. (c). Pressure dependence of the unit-cell parameter in experiment (symbols) and calculation (line). (d) pressure dependence of the unit-cell volume in experiment (symbols) and calculation (lines).

Calculated I -O bond distance under pressure

Calculated pressure dependence of I-O bond distance, solid line is for LP and dash line is for HP phase

HP Infrared

(a). IR spectra of Fe(IO$_3$)$_3$ at ambient pressure, background was subtracted manually, the Gaussians was used for the fits. (b). IR spectra at different pressure which are indicted in GPa, the asterisks indicate the different phonons, red arrows show the changes at the phase transition while the black arrows show the peak evolution in LP phase. (c). Pressure dependence of the IR modes obtained from experiments, filled and empty symbols are used for E$_1$ and A modes, respectively.

Calculated pressure dependence of vibration modes

(a). Calculated pressure dependence of the Raman and IR-active modes (A and E$_1$ modes, filled and empty symbol are used for E$_1$ and A modes, respectively). (b) calculated pressure dependence of Raman-active modes only (E2 mode).

Conclusion

1. Pressure induced phase transition on Fe(IO$_3$)$_3$ happened at 22 GPa in HP XRD and 15 GPa in HP IR, different phase transition pressure is because of different PTM.
2. According to the refinement of the HP XRD spectra, the HP phase can be described in the same space group as the LP phase, P6$_3$.
3. The phase transition accompanied by a gradually increase of the coordination of I atoms, which is due to the lone-pair electrons existed in I atoms.
4. The phase transition companied by a substantial c/a ratio and a volume collapse large than 5%. The nature of the phase transition is first-order.
5. The bulk modules of the LP and HP phase were B_0=55(2) GPa and B_0=73 GPa in experiment and B_0=36(1) GPa and B_0= 48(3) GPa in calculation.

Acknowledgements

We thanks the financial support given by the Spanish Ministry of Science, Innovation and Universities under Grant Nos. PID2019-106383GB-C41 and RED2018-102612-T (MALTA Consolider-Team) and by Generalitat Valenciana under Grant Prometeo/2018/123 (EFIMAT). A. L and D. E also thank the Generalitat Valenciana for the PH.D. fellowship GRISOLIAP/2019/025.

FIRST-ORDER ISOSTRUCTURAL PHASE TRANSITION INDUCED BY HIGH-PRESSURE IN Fe(IO$_3$)$_3$

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Metal iodates has been studied at ambient pressure because of their dielectric, magnetic, or nonlinear optical properties. Many of them have been also studied for the reason that they are superionic conductors, which make them excellent barocaloric materials, very promising for the development of ecofriendly solid-state cooling technologies. High-pressure (HP) research is known to be an efficient tool to determine the characteristics of materials. Among iodates, only LiIO3, KIO3, and AgIO3 have been studied under HP. No phase transitions have been found in LiIO3 up to 73 GPa. In contrast, KIO3 shows phase transitions at 7 and 14 GPa. On the other hand, in AgIO3 a new phase was found at 2.7 GPa and 240 °C. These facts suggest that the HP behavior of metal iodates can be extremely complex and should be further studied.

Here, we have studied the HP behavior of Fe(IO$_3$)$_3$ at RT up to 35 GPa using powder XRD, infrared and Raman micro-spectroscopy, and density-functional theory (DFT) calculations. We have found evidence of a pressure-induced structural phase transition at 15 - 22 GPa. Powder XRD was used to obtain the structure of the HP phase, which can be described by the same space group (P63) than the low-pressure (LP) phase but with a substantial different c/a ratio. This is supported by our computational simulations. The phase transition involves a large volume collapse and a change in the coordination polyhedron of iodine, being a first-order transition. It also produces substantial changes in the infrared and Raman spectra. The pressure dependence of phonon frequencies and unit-cell parameters have been obtained. A mode assignment is proposed for phonons. The bulk modulus of the two phases was obtained resulting in B_0 = 55(2) GPa for the LP phase and B0 = 82(9) GPa for the HP phase. The results are compared with other iodates, in particular LiIO$_3$, for which we have also performed DFT calculations. A possible mechanism driving the observed phase transition is discussed. In particular, we conclude that pressure triggers the phase transition by favoring the linking of one of the lone electron pairs of iodine to one oxygen atom in the nearest IO$_3$ unit.

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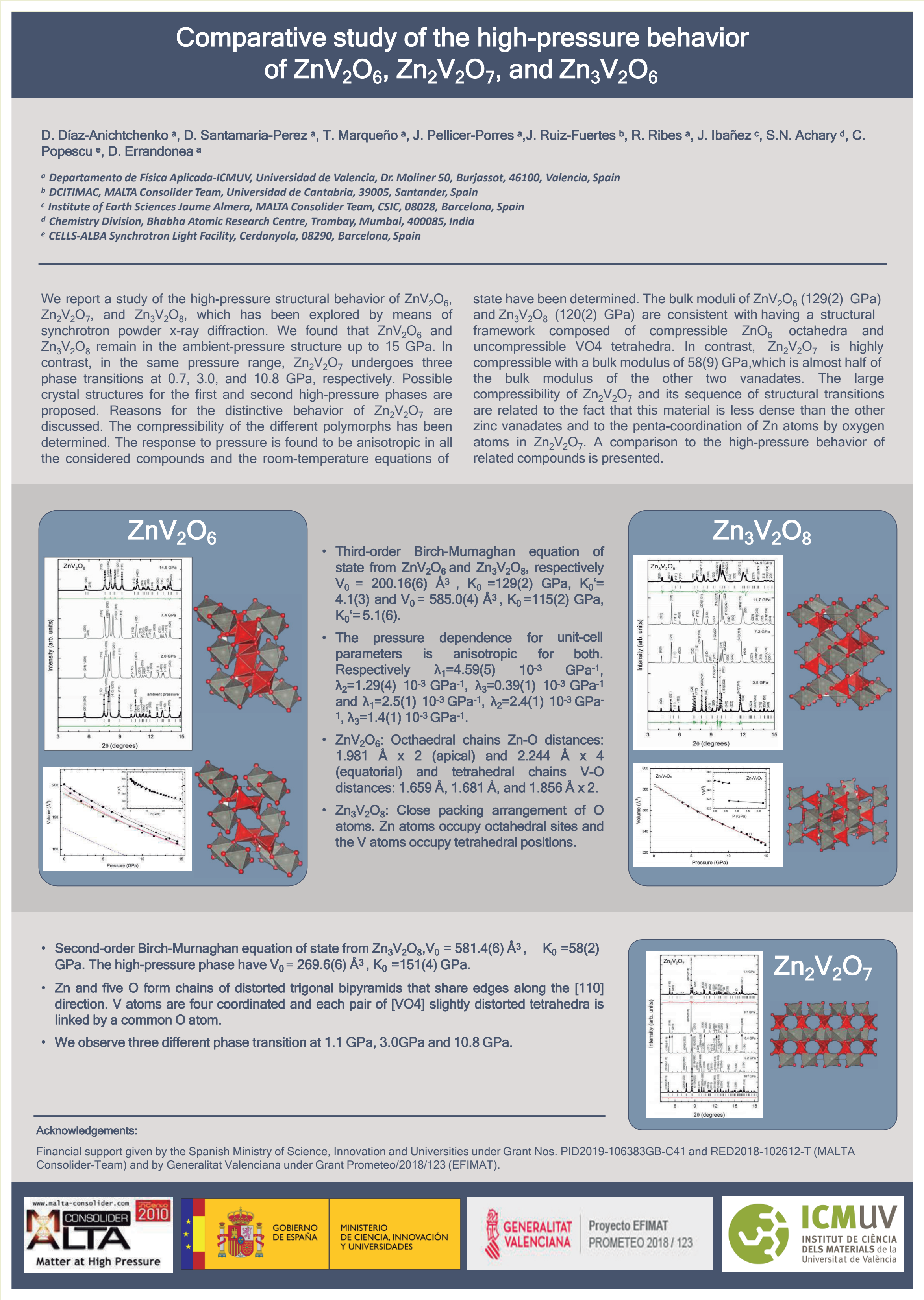

Comparative study of the high-pressure behavior of ZnV_2O_6, $Zn_2V_2O_7$, and $Zn_3V_2O_6$

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We report a study of the high-pressure structural behavior of ZnV_2O_6, $Zn_2V_2O_7$, and $Zn_3V_2O_8$, which has been explored by means of synchrotron powder x-ray diffraction. We found that ZnV_2O_6 and $Zn_3V_2O_8$ remain in the ambient-pressure structure up to 15 GPa. In contrast, in the same pressure range, $Zn_2V_2O_7$ undergoes three phase transitions at 0.7, 3.0, and 10.8 GPa, respectively. Possible crystal structures for the first and second high-pressure phases are proposed. Reasons for the distinctive behavior of $Zn_2V_2O_7$ are discussed. The compressibility of the different polymorphs has been determined. The response to pressure is found to be anisotropic in all the considered compounds and the room-temperature equations of state have been determined. The bulk moduli of ZnV_2O_6 (129(2) GPa) and $Zn_3V_2O_8$ (120(2) GPa) are consistent with having a structural framework composed of compressible ZnO_6 octahedra and uncompressible VO4 tetrahedra. In contrast, $Zn_2V_2O_7$ is highly compressible with a bulk modulus of 58(9) GPa,which is almost half of the bulk modulus of the other two vanadates. The large compressibility of $Zn_2V_2O_7$ and its sequence of structural transitions are related to the fact that this material is less dense than the other zinc vanadates and to the penta-coordination of Zn atoms by oxygen atoms in $Zn_2V_2O_7$. A comparison to the high-pressure behavior of related compounds is presented.

ZnV_2O_6

- Third-order Birch-Murnaghan equation of state from ZnV_2O_6 and $Zn_3V_2O_8$, respectively V_0 = 200.16(6) $Å^3$, K_0 =129(2) GPa, K_0'= 4.1(3) and V_0 = 585.0(4) $Å^3$, K_0 =115(2) GPa, K_0'= 5.1(6).
- The pressure dependence for unit-cell parameters is anisotropic for both. Respectively λ_1=4.59(5) 10^{-3} GPa^{-1}, λ_2=1.29(4) 10^{-3} GPa^{-1}, λ_3=0.39(1) 10^{-3} GPa^{-1} and λ_1=2.5(1) 10^{-3} GPa^{-1}, λ_2=2.4(1) 10^{-3} GPa^{-1}, λ_3=1.4(1) 10^{-3} GPa^{-1}.
- ZnV_2O_6: Octhaedral chains Zn-O distances: 1.981 Å x 2 (apical) and 2.244 Å x 4 (equatorial) and tetrahedral chains V-O distances: 1.659 Å, 1.681 Å, and 1.856 Å x 2.
- $Zn_3V_2O_8$: Close packing arrangement of O atoms. Zn atoms occupy octahedral sites and the V atoms occupy tetrahedral positions.

$Zn_3V_2O_8$

- Second-order Birch-Murnaghan equation of state from $Zn_3V_2O_8$,V_0 = 581.4(6) $Å^3$, K_0 =58(2) GPa. The high-pressure phase have V_0 = 269.6(6) $Å^3$, K_0 =151(4) GPa.
- Zn and five O form chains of distorted trigonal bipyramids that share edges along the [110] direction. V atoms are four coordinated and each pair of [VO4] slightly distorted tetrahedra is linked by a common O atom.
- We observe three different phase transition at 1.1 GPa, 3.0GPa and 10.8 GPa.

$Zn_2V_2O_7$

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HIGH-PRESSURE BEHAVIOR OF ZnV_2O_6, $Zn_2V_2O_7$, and $Zn_3V_2O_8$

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Vanadium oxide-based materials are currently receiving substantial attention due to their exceptional physical and chemical properties, which make them useful for many technological applications. In addition to the technological interests, these compounds are also interesting from a fundamental point of view. In special, their diverse stoichiometry gives the possibility to make a systematic comparison of their crystal structures and high-pressure (HP) behavior.

We have performed a comparative study of the room-temperature HP behavior of ZnV_2O_6, $Zn_2V_2O_7$, and $Zn_3V_2O_8$. In particular, their structural stability has been studied by synchrotron powder XRD. Experiments were carried out using diamond-anvil cells at ALBA synchrotron (MSPD Beamline). We have found that the ambient- pressure polymorphs of ZnV_2O_6 and $Zn_3V_2O_8$ remain stable up to 15 GPa. In contrast, $Zn_2V_2O_7$ undergoes at least three phase transitions in the same pressure range. The transition pressures are 1.1, 3.8, and 10.8 GPa.

From the XRD measurements we have determined the crystal structure of the different HP polymorphs of $Zn_2V_2O_7$. We have also determined the axial and bulk compressibilities of all the studied compounds. In particular, room-temperature P-V equations of state have been determined and for monoclinic structures, the isothermal compressibility tensor has been obtained; including the principal axes of compression. All these results will be presented in this poster.

Among other interesting results, we have found that the bulk modulus changes considerably among different vanadates. In particular, ZnV_2O_6 and $Zn_3V_2O_8$ have a bulk modulus of 129 and 120 GPa, respectively. However, $Zn_2V_2O_7$ is extremely compressible with a bulk modulus of 58 GPa. Reasons for this "anomalous" compressibility of $Zn_2V_2O_7$ and the existence of multiple phase transitions on this compound will be presented. We will also compare our results with the literature and with related compounds. A systematic analysis of all the available information suggests that polyhedral networks of the different vanadates have a substantial influence in their HP behavior. In particular, the penta-coordination of Zn atoms in $Zn_2V_2O_7$ is what makes this compound to behave differently than other vanadates. Predictions of the HP behavior of $Zn_4V_2O_9$ will be commented too.

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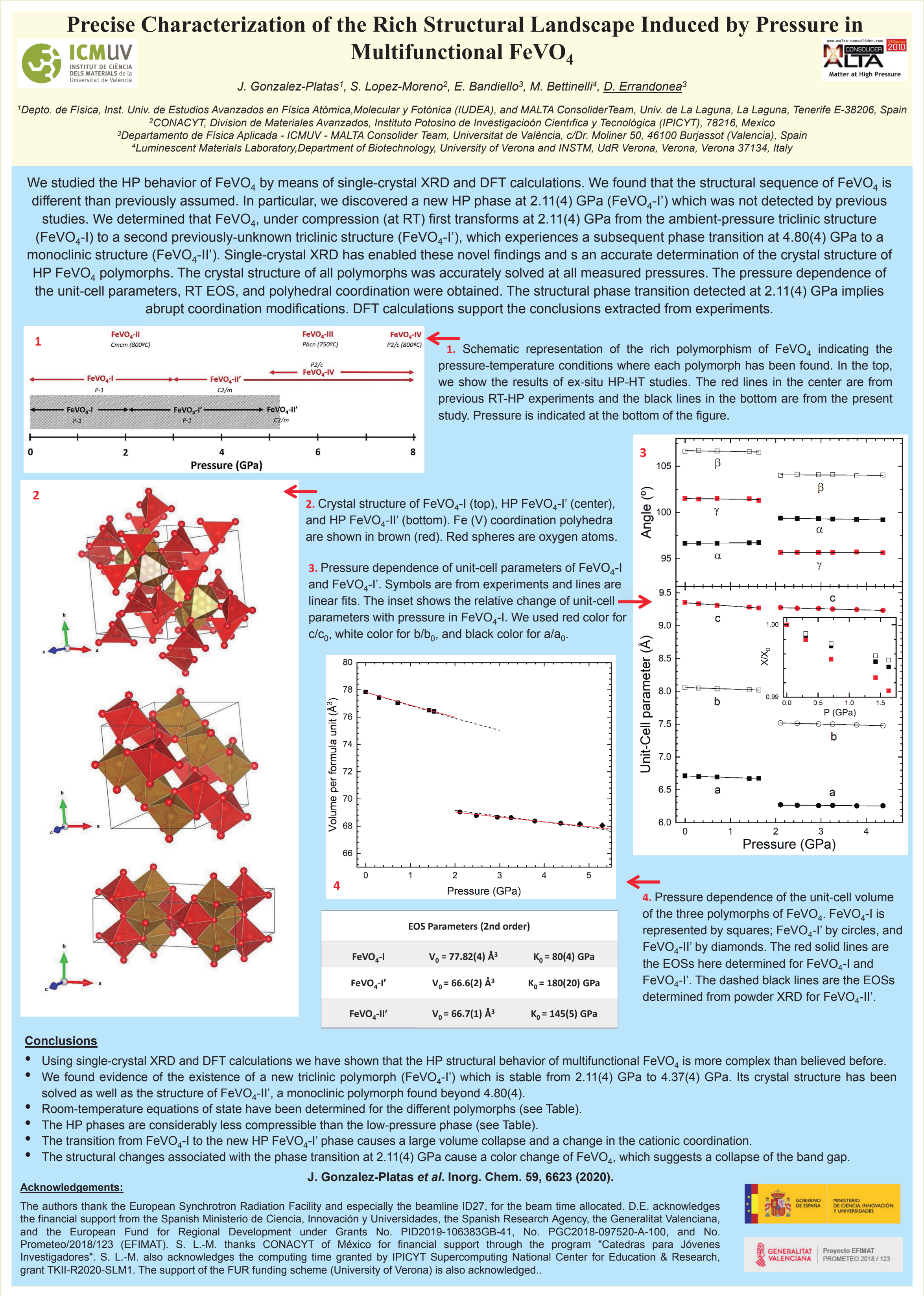

Precise Characterization of the Rich Structural Landscape Induced by Pressure in Multifunctional $FeVO_4$

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We studied the HP behavior of $FeVO_4$ by means of single-crystal XRD and DFT calculations. We found that the structural sequence of $FeVO_4$ is different than previously assumed. In particular, we discovered a new HP phase at 2.11(4) GPa ($FeVO_4$-I') which was not detected by previous studies. We determined that $FeVO_4$, under compression (at RT) first transforms at 2.11(4) GPa from the ambient-pressure triclinic structure ($FeVO_4$-I) to a second previously-unknown triclinic structure ($FeVO_4$-I'), which experiences a subsequent phase transition at 4.80(4) GPa to a monoclinic structure ($FeVO_4$-II'). Single-crystal XRD has enabled these novel findings and s an accurate determination of the crystal structure of HP $FeVO_4$ polymorphs. The crystal structure of all polymorphs was accurately solved at all measured pressures. The pressure dependence of the unit-cell parameters, RT EOS, and polyhedral coordination were obtained. The structural phase transition detected at 2.11(4) GPa implies abrupt coordination modifications. DFT calculations support the conclusions extracted from experiments.

1. Schematic representation of the rich polymorphism of $FeVO_4$ indicating the pressure-temperature conditions where each polymorph has been found. In the top, we show the results of ex-situ HP-HT studies. The red lines in the center are from previous RT-HP experiments and the black lines in the bottom are from the present study. Pressure is indicated at the bottom of the figure.

2. Crystal structure of $FeVO_4$-I (top), HP $FeVO_4$-I' (center), and HP $FeVO_4$-II' (bottom). Fe (V) coordination polyhedra are shown in brown (red). Red spheres are oxygen atoms.

3. Pressure dependence of unit-cell parameters of $FeVO_4$-I and $FeVO_4$-I'. Symbols are from experiments and lines are linear fits. The inset shows the relative change of unit-cell parameters with pressure in $FeVO_4$-I. We used red color for c/c_0, white color for b/b_0, and black color for a/a_0.

4. Pressure dependence of the unit-cell volume of the three polymorphs of $FeVO_4$. $FeVO_4$-I is represented by squares; $FeVO_4$-I' by circles, and $FeVO_4$-II' by diamonds. The red solid lines are the EOSs here determined for $FeVO_4$-I and $FeVO_4$-I'. The dashed black lines are the EOSs determined from powder XRD for $FeVO_4$-II'.

EOS Parameters (2nd order)		
$FeVO_4$-I	V_0 = 77.82(4) Å^3	K_0 = 80(4) GPa
$FeVO_4$-I'	V_0 = 66.6(2) Å^3	K_0 = 180(20) GPa
$FeVO_4$-II'	V_0 = 66.7(1) Å^3	K_0 = 145(5) GPa

Conclusions

- Using single-crystal XRD and DFT calculations we have shown that the HP structural behavior of multifunctional $FeVO_4$ is more complex than believed before.
- We found evidence of the existence of a new triclinic polymorph ($FeVO_4$-I') which is stable from 2.11(4) GPa to 4.37(4) GPa. Its crystal structure has been solved as well as the structure of $FeVO_4$-II', a monoclinic polymorph found beyond 4.80(4).
- Room-temperature equations of state have been determined for the different polymorphs (see Table).
- The HP phases are considerably less compressible than the low-pressure phase (see Table).
- The transition from $FeVO_4$-I to the new HP $FeVO_4$-I' phase causes a large volume collapse and a change in the cationic coordination.
- The structural changes associated with the phase transition at 2.11(4) GPa cause a color change of $FeVO_4$, which suggests a collapse of the band gap.

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PRECISE CHARACTERIZATION OF THE RICH STRUCTURAL LANDSCAPE INDUCED BY PRESSURE IN MULTIFUNCTIONAL $FeVO_4$

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Currently, there is an increase in the requirement of materials suitable for green technologies. These include energy-storage devices, sustainable and nonconventional energy sources, low-consuming electronics, and information-storage appliances. $FeVO_4$ has many interesting electronic and magnetic properties, which make it suitable for these applications. As a consequence, it is considered as a dream material for developing multiple non-contaminant technologies. In particular, because of its optical band gap (2.3 eV), $FeVO_4$ is a superlative semiconductor for the clean production of hydrogen from solar energy via photocatalytic water splitting. Many of the properties of $FeVO_4$ can be tuned for its different technological applications by means of structural phase transitions. These transitions can be triggered by the application of high pressure (HP), resulting in changes in the optical, electrical, vibrational, mechanical, and structural properties.

In this poster we present results obtained under compression in $FeVO_4$ by means of single-crystal XRD and density functional theory (DFT) calculations. We have found that the structural sequence of $FeVO_4$ is different from that previously assumed. In particular, we have discovered a new HP phase at 2.1 GPa which was not detected by previous powder XRD studies. We have determined that $FeVO_4$ first transforms at 2.1 GPa from the ambient-pressure triclinic to a second previously unknown triclinic structure, which experiences a subsequent phase transition at 4.8 GPa to a monoclinic structure. Single-crystal XRD has enabled these novel findings as well as an accurate determination of the crystal structure of $FeVO_4$ polymorphs under HP conditions. The crystal structure of all polymorphs has been accurately solved at all measured pressures. The pressure dependence of the unit-cell parameters and polyhedral coordination has been obtained The room- temperature equation of state and the principal axes of the isothermal compressibility tensor have also been determined. DFT calculations support the conclusions extracted from experiments.

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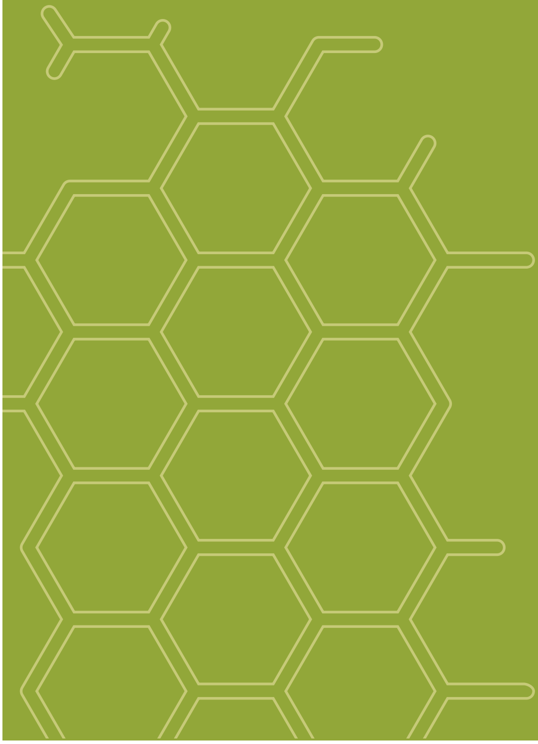

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