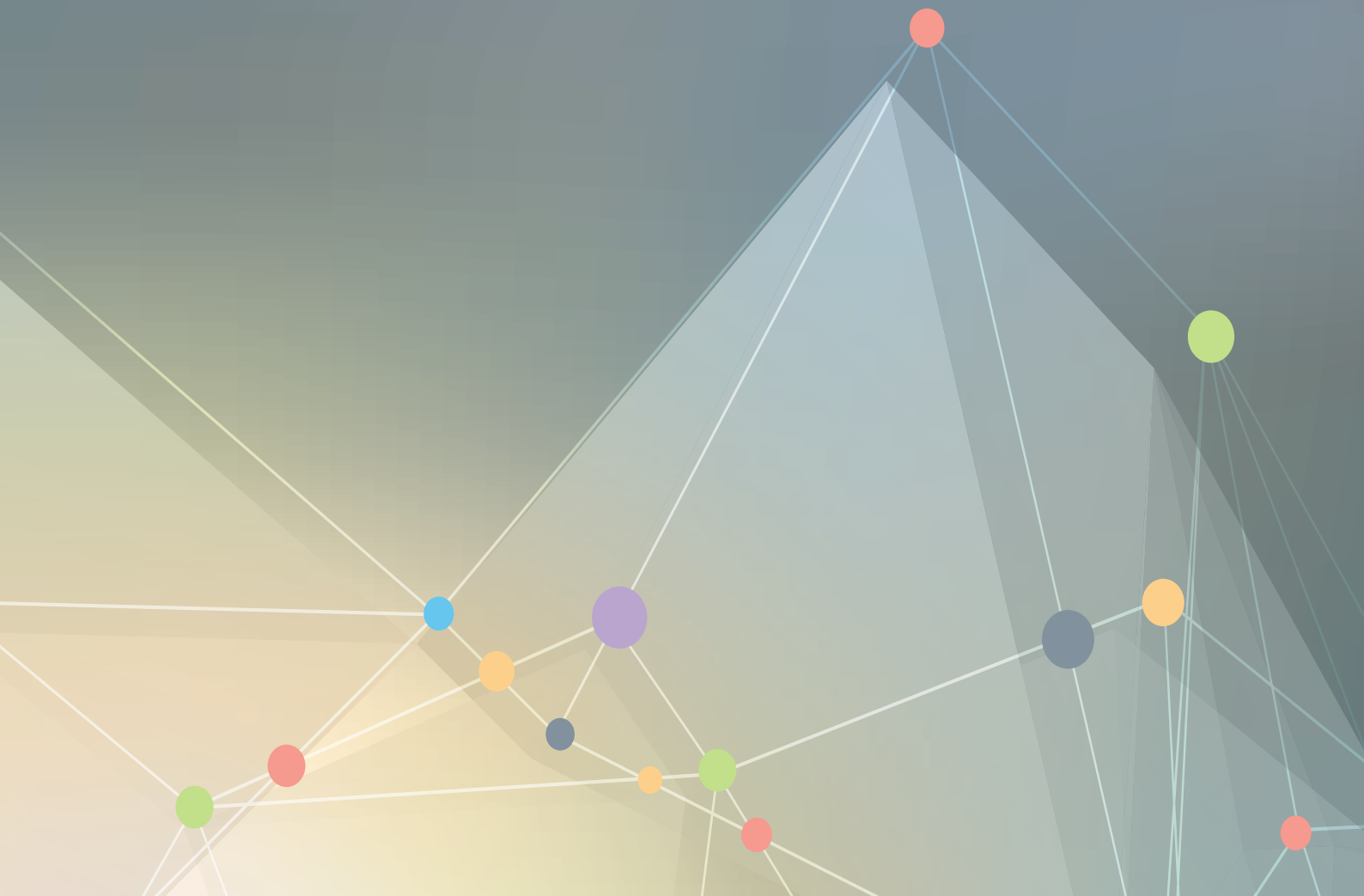


# BOOK OF ABSTRACTS

## Poster Presentations



# POSTERS AREA 1

A1

*Check the map at the end of the document*

## Thematic sessions

- Nanochemistry, Nanoparticles, Nanocatalysis
  - Nanomaterials for energy
- Nanotechnology for cleaning environment
  - Nanobiosciences

# List of Poster Presentations

AREA - 1

## A1 - NANOCHEMISTRY | NANOMATERIALS FOR ENERGY | CLEANING ENVIRONMENT | NANOBIOSCIENCES

A1-01	Development of Efficient Routes for the Synthesis of Alumina Supported Non-Noble Metal Nanoparticles	Abdenmour BENABBAS • CNRS - IC2MP, France
A1-02	Ecologically efficient synthesis of heterogeneous catalysts via solvent-free reactive extrusion	Ryma HADDAD • Sorbonne Univ. - LCMCP, France
A1-03	Emulsion processing of gold nanoparticle shells: towards plasmonic nanoresonators	MouktarNOUR MAHAMOUD • CNRS - ISCR, France
A1-04	Förster resonance energy transfer between multicolor fluorescent carbon dots	Vladimir LYSENKO • CNRS - ILM, France
A1-05	Induction of chirality in semiconductor CdSe nanoplatelets	Guillaume LANDABURU • CNRS - LCH, France
A1-06	Influence of heteroelement addition on the properties of nanostructured titania	Jean-Luc BLIN • Univ. of Lorraine - L2CM, France
A1-07	Innovation for resolute size distribution measurement of nanocarriers and bioconjugates in native state	Cédric SARRAZIN • Nanoscale Metrix, France
A1-08	LaPO <sub>4</sub> :Eu nanorods as polarized luminescence emitters and their application for in situ flow shear monitoring in an energy harvesting device	Lilian MAGERMANS • EP - LPMC, France
A1-09	Luminescence impact on green silver sulfide (Ag <sub>2</sub> S) nanothermometer with hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	Thomas NAILLON • Sorbonne Univ. - LCMCP, France
A1-10	Micropore 3D graphenes: circumventing essential issues in large scale synthesis	Steven COMPERE • Univ. Poitiers - IC2MP, France
A1-11	New boron phosphide nanocrystals synthesized in molten salt	Amandine SENE • CNRS - LCMCP, France
A1-12	Optimization of a LSPR Sensor Chip Using Hollow Au Nanoparticles	Daoming SUN • Sorbonne Univ. - LRS, France
A1-13	Optimization of anisotropic LaPO <sub>4</sub> :Eu <sup>3+</sup> nanorods as polarized luminescence probes in fluid flow	Qilin ZOU • CNRS - LPMC, France
A1-14	Reactivités chimiques entre les imogolites hybrides et une phase cimentaire : formulation d'une matrice de conditionnement pour la stabilisation des déchets nucléaires	Estelle PUEL • CEA - NIMBE, France
A1-15	Screening of nanoporous carbon electrodes for the electrochemical conversion of CO <sub>2</sub> and N-compounds.	Ali FAYAD • Univ. Orléans - CEMHTI, France
A1-16	Structural disorder and vibrational properties of transition aluminas	Iñigo GONZALEZ DE ARRIETA • Univ. Basque Country - CEMHTI, France
A1-17	Studying dynamics of molecular layers covering gold nanostructures by SERS	Danilo OLIVEIRA DE SOUZA • Univ. Lille - UCCS, France
A1-18	Synthesis and Colloidal Stabilization of Manganese and Zinc Ferrite Magnetic Nanoparticles for failsafe Magnetocuring of resins	Naoures HMILI • Sorbonne Univ. - LRS, France
A1-19	Synthesis of Carbon Quantum Dots for Anti-counterfeiting	Théo DUARTE • UTT - L2n, France
A1-20	Synthesis of core-shell and nanoalloys from immiscible Cu and Co elements; application in dehydrogenation catalysis	Lorette SICARD • Univ. Paris Cité - ITODYS, France
A1-21	Synthesis of Mesoionic Carbene (MIC) Stabilized Gold Nanoparticles from 1,2,3-Triazolium Salts	Salem Saleh BA SOWID • Sorbonne Univ. - LCMCP, France
A1-22	Understanding the interactions in CuO-ZnO-ZrO <sub>2</sub> catalyst	Ksenia PARKHOMENKO • CNRS - ICPEES, France
A1-23	Understanding the mechanisms involved in the formation of silicon particles from the thermal decomposition of hydrogen silsesquioxane: an in situ study by ETEM	Cynthia CIBAKA NDAYA • CNRS - ICMCB, France
A1-24	Using Mo(0) complex as highly reactive platform for the synthesis of molybdenum oxide nanoparticles under mild conditions	Martin JAKOObI • CNRS - LCC, France
A1-25	Improving electrical contact of highly n-type doped 4H-SiC by Circular Transfer Length Method	Lazar MIHAI • CNRS- L2n, France
A1-26	Catalytic NO <sub>x</sub> treatment from hydrogen internal combustion engine	Amira BEN ATTIA • CNRS - IC2MP, France

# List of Poster Presentations

AREA - 1

## A1 - NANOCHEMISTRY | NANOMATERIALS FOR ENERGY | CLEANING ENVIRONMENT | NANOBIOSCIENCES

A1-27	Development and in vitro analysis of SPIO for theranostic purposes in cancer	Chloé GERVASONI • <i>SON SAS, France</i>
A1-28	DNA biodetection assay based on Whispering Gallery Mode Energy Transfer	Nour ALKASTNTINI • <i>ESPCI Paris /PSL - LPEM, France</i>
A1-29	Magneto-plasmonic biosensing: from benchtop spectrometer readout to 3D-printed microfluidic devices	Walid AIT MAMMAR • <i>Sorbonne Univ. - LRS, France</i>
A1-30	SPR Biosensor for the detection of micro-RNAs	Coline BELTRAMI • <i>Univ. Paris Saclay - LCF, France</i>

**Thematic session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Nanochemistry, Control of particle size, Wet Synthesis, Supported metallic nanoparticles

**Disciplinary fields involved:** Chemistry, Material Sciences

## Development of Efficient Routes for the Synthesis of Alumina Supported Non-Noble Metal Nanoparticles

Abdenour BENABBAS<sup>1</sup>, Catherine ESPECEL<sup>1</sup>, Anthony LE VALANT<sup>1</sup>, Christian RICOLLEAU<sup>2</sup>, Guillaume WANG<sup>2</sup>, Tzonka MINEVA<sup>3</sup>, Jaysen NELAYAH<sup>2</sup>, Hazar GUESMI<sup>3</sup>, Florence EPRON<sup>1</sup>

1. CNRS, Université de Poitiers, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), Poitiers, France

2. Université Paris Cité, CNRS, Laboratoire Matériaux et Phénomènes Quantiques (MPQ), Paris, France

3. CNRS, Université de Montpellier, ENSCM, Institut Charles Gerhardt de Montpellier (ICGM), Montpellier, France

Reducing the amount of expensive noble metals without affecting the catalytic efficiency is a new trend in the development of novel heterogeneous catalysts. For instance, promising catalytic properties in dehydrogenation reactions, such as propane dehydrogenation reaction, are expected for the system **Pt-M/Al<sub>2</sub>O<sub>3</sub>** prepared by dispersing ultra-small amounts of **Pt** on the surface of a host non-noble metal **M** (acting as promoter of Pt).

Comparing the catalytic properties of **Pt-M/Al<sub>2</sub>O<sub>3</sub>** needs the successful synthesis of the system **M (= Cu, Sn or Ga)/Al<sub>2</sub>O<sub>3</sub>**, which is already quite challenging due to the difficulty to reduce these non-noble metals and to obtain particle in the same size range. Thus, the poster will be dedicated to the first part of this project aiming to develop easy and cheap methods for the preparation of stable homogeneous promoter **M<sup>0</sup>** nanoparticles of small size (5-10 nm) dispersed on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Conventional wet synthesis routes such as microsuspension in water and polyol are selected. The effect of the experimental parameters (ex: temperature, reducing agent, precursor, pH, capping agents, etc) will be reported. A special attention will be paid to the characterization of the chemical and structural properties of these materials, their surface accessibility and their stability under synthesis and catalytic test conditions.

### References:

1. H. Kawasaki, Y. Kosaka, Y. Myoujin, T. Narushima, T. Yonezawa and R. Arakawa, Chem. Commun., 2011, 47, 7740–7742

2. M. Samim, N. K. Kaushik and A. Maitra, Bull. Mater. Sci., Vol. 30, No. 5, October 2007, pp. 535–540

### Acknowledgements:

This project is named BINOME (PhD within). It is funded by the French Agence Nationale de la Recherche (ANR). Project ID: **ANR-21-CE07-0029**.

This work is supported by the French government program "Investissements d'Avenir" (**EUR INTREE, reference ANR-18-EURE-0010**)



**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** green synthesis, solvent-free sol-gel, alumina, ruthenium, catalysis

**Disciplinary fields involved:** Materials physic and chemistry

**Sustainable Development Goals\* eventually involved in your research:** Responsible consumption and production (Goal 12)

## Ecologically efficient synthesis of heterogeneous catalysts via solvent-free reactive extrusion

Ryma Haddad <sup>1</sup>, Pierre-Igor Dassie <sup>1</sup>, Clément Sanchez <sup>1,2</sup>, Damien Debecker <sup>3</sup>,  
Corinne Chanéac <sup>1</sup> Cédric Boissière <sup>1</sup>

1. *Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université, Paris, France*

2. *Collège de France, Paris France*

3. *Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCLouvain), Louvain-La-Neuve, Belgium*

### Abstract

We present a new strategy for the synthesis of sustainable manufacturing catalysts that complies the 12<sup>th</sup> goal of the UN on responsible consumption and production. To achieve that we combine the sol-gel process with the principle of reactive extrusion. This method allows simultaneously the formation and shaping of the active phase and the support, at room temperature in a solvent-free continuous mode. Reactive extrusion has been intensively developed for the synthesis and processing of polymeric materials but it is still in its beginning stage for metal oxides <sup>[1]</sup>

We focused on the synthesis of bohemite ( $\gamma$ -AlOOH) which is converted upon calcination into mesoporous alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) with high specific surface area. This oxide is widely used in industry as catalyst and catalyst support. As-obtained material exhibits good catalytic properties regarding ethanol dehydration activity comparable to those observed in literature. Afterwards, we developed reactors and processes for the synthesis of Ruthenium-based catalysts supported on  $\gamma$ -AlOOH and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> methanation. In order to quickly evaluate the influence of the experimental parameters (concentrations, temperature and hydrolysis), the simultaneous synthesis of the support and the active phase of the catalyst was developed in a stirred reactor tank (outside the extruder). The Ru precursor is mixed with the Al precursor without addition of solvent then the mixture was hydrolyzed with a stoichiometric quantity of water. Ru/AlOOH catalysts with Ru weight contents wt%Ru 2 and 6% were prepared. The obtained materials exhibit dispersed Ru clusters and NPs of 3-5 nm on  $\gamma$ -AlOOH with promising CO<sub>2</sub> methanation activity: 100% CH<sub>4</sub> selectivity with a production rate of 33 mmol.g<sup>-1</sup>.h<sup>-1</sup> and a conversion upper to 66% at 300 °C catalysis temperature (for wt%Ru 6% reduced at 200 °C).

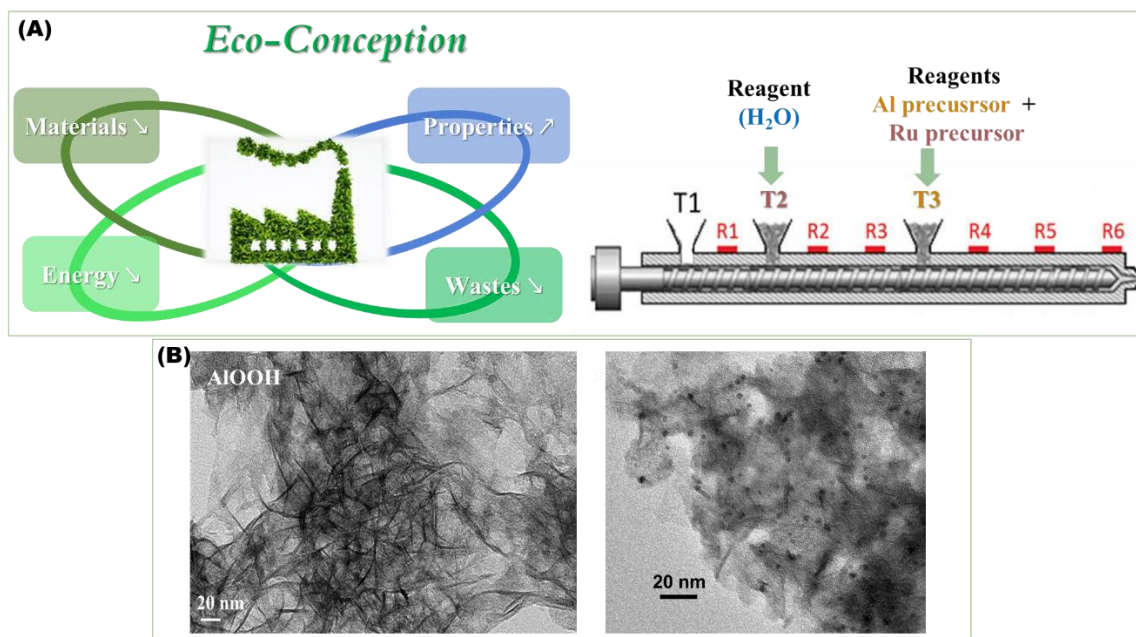


Figure 1 (A) Sustainable approach to reduce the environmental impact of shaping catalyst synthesis at left, and scheme of the experimental set-up of reactive extrusion at right; (B) TEM images of  $\gamma$ -AlOOH synthesized by solvent-free reactive extrusion at left and Ru/AlOOH (Wt% Ru = 6%) at right prepared by solvent-free synthesis in a stirred reactor tank

**Reference:**

[1] Crawford, D.; Casaban, J.; Haydon, R.; Giri, N.; McNally, T.; James, S. L. (2015). Chem. Sci. 6 (3), 1645–1649.

# 2023

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** formulation, nanomaterials, optics-plasmonics

**Disciplinary fields involved:** Chemistry, Physics

**Sustainable Development Goals\* eventually involved in your research:** -

## Emulsion processing of gold nanoparticle shells: towards plasmonic nanoresonators

**Mouktar NOUR<sup>1</sup>, Alexandre BARON<sup>2</sup>, Virginie PONSINET<sup>2</sup> et Fabienne GAUFFRE<sup>1</sup>.**

1. Univ Rennes, CNRS, ISCR – UMR 6226, ScanMat – UAR 2025, F-35000 Rennes, France

2. Univ. Bordeaux, Centre de Recherche Paul Pascal, CNRS UMR 5031, 115 Avenue Schweitzer, 33600 Pessac, France

The chemistry of metallic nanoparticles, and more specifically that of noble metals, is a rapidly expanding field (1). The elaboration of well-ordered assemblies of nanoparticles by solution routes remains an experimental challenge, with a wide potential of applications. In the case of metallic gold or silver nanoparticles, electromagnetic effects resulting from plasmonic coupling between the nanoparticles are expected. In particular, "hollow" spherical assemblies of such nanoparticles can constitute plasmonic nanoresonators capable of interacting with the magnetic component of light, a phenomenon that does not exist in natural materials. Such nanoresonators are being considered as the building blocks for the development of metamaterials.

Our team has developed a process for the formulation of nanoparticle shells, based on an unconventional emulsification (spontaneous and without surfactant): The Ouzo effect.(2) This strategy allows the assembly of nanoparticles around droplets of about 100nm in diameter, with excellent size homogeneity. However, this has not been achieved with gold yet.

The objective of this work is to understand the physico-chemical mechanisms involved in the formation of gold NP-shells in order to develop metamaterials and to explore their applications.

The first part is devoted to the study of the ouzo ternary system "water/THF/BHT" allowing the realization of NP-shells.(3) In addition, we investigate the use of gold nanoparticles of various sizes that have been synthesised in oleylamine. Furthermore, the idea is not only to assemble the gold nanoparticles around the ouzo drops but also to control the distance between them by substitutions in situ with shorter ligands in order to have plasmonic coupling, which is necessary to obtain the desired optical properties.



## References:

1. Aurelie Féré Paquirissamy. *Nano-objets hybrides et polymères sous irradiation. Chimie inorganique. Université Paris Saclay (COmUE), 2016. Français. NNT : 2016SACLS390. tel-01444882.*
2. Sciortino F, Thivolle M, L. Kahn M, Gaillard C, Chevance S, Gauffre F. *Structure and elasticity of composite nanoparticle/polymer nanoshells (hybridosomes®). Soft Matter. 2017;13(24):4393-400.*
3. Iglicki D, Goubault C, Nour Mahamoud M, Chevance S, Gauffre F. *Shedding light on the formation and stability of mesostructures in ternary "Ouzo" mixtures. J Colloid Interface Sci. 1 mars 2023;633:72-81.*

**Thematic Session :** *Nanochemistry, Nanoparticles, Nanocatalysis*

**Keywords:** carbon nanodots, photoinduced electronic transitions, fluorescence, resonant energy transfer, cell fluorescence imaging

**Disciplinary fields involved :** Physics, Chemistry, Biology

**Sustainable Development Goals\* eventually involved in your research:** Good health and well-being (Goal 3)

## Förster resonance energy transfer between multicolor fluorescent carbon dots

Ivan Lysenko<sup>1</sup>, Alexander Zaderko<sup>2,3</sup>, Alain Gélöën<sup>4</sup>, Tetyana Nychporuk<sup>5</sup>, Valeriy Skryshevsky<sup>2,3</sup> and Vladimir Lysenko<sup>6</sup>

1. *Physics Department, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine*
2. *Institute of High Technologies, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine*
3. *Corporation Science Park, Taras Shevchenko University of Kyiv, Kyiv, Ukraine*
4. *UMR Ecologie Microbienne Lyon (LEM), CNRS 5557, INRAE 1418, Claude Bernard University of Lyon, Villeurbanne, France*
5. *Lyon Institute of Nanotechnologies, UMR CNRS 5270, INSA de Lyon, Villeurbanne, France*
6. *Light Matter Institute, UMR CNRS 5306, Claude Bernard University of Lyon, Villeurbanne, France*

Scientific interest in carbon nanodots (CNDs) began to grow exponentially since 2004, when pronounced fluorescent properties of carbon-based nanomaterials have been reported [1]. Since then, a variety of CNDs characterized by a high quantum yield of fluorescence, high biocompatibility and low toxicity for living organisms were chemically synthesized [2]. CNDs are ideally suited for multidisciplinary applications in various fields of science and technology, such as, for example: photonics, imaging of biological objects, medicine, sensors and others [3]. In our work, optical properties of CNDs chemically synthesized by solvothermal methods were studied. Optical absorption, photoluminescence excitation (PLE) and emission (PL) spectra as well as the characteristic photoluminescence lifetimes (7-11 ns) were measured. The studied concentration dependences of PL/PLE maps of the CNDs allowed to illustrate the phenomenon of resonant energy transfer of electronic excitation according to Förster mechanism (FRET). Temperature and pH dependences of the PL/PLE-maps of CNDs colloids allowed to confirm the FRET effect. The possibility of CNDs application for multicolor cell fluorescence imaging were also shown.

**References** [1] R., Gu Y., et al., *J. Am. Chem. Soc.*, **126**, (2004), p. 12736.

[2] Speranza G., *Nanomaterials*, **11**, 967 (2021).

[3] Liu J., Li R., Yang B., *ACS Cent. Sci.*, **6**, (2020) p. 2179

**Acknowledgment:** This work was funded by the European Community, Program H2020-MSCA-RISE-2020, project №101008159 “UNAT”

**Thematic Session :** Nanophotonics and nano-optics

**Keywords:** Nanoparticles, semiconductors, chirality

**Disciplinary field involved :** Chemistry

**Sustainable Development Goals\* eventually involved in your research:** Industry, innovation & infrastructure (Goal 9)

## Induction of chirality in semiconductor CdSe nanoplatelets

Landaburu Guillaume<sup>1</sup>, Benjamin Abécassis<sup>1</sup>

1. Univ. Lyon, ENS de Lyon, CNRS, Laboratoire de Chimie, Lyon, France

The recent trend of research surrounding chiral nanoparticles has given birth to a variety of chiral semiconductors, extending their potential applications to the fields of chiral detection, enantioselective catalysis, spintronics, ... The first synthesis of chiral semiconductors<sup>[1]</sup> was performed by the grafting of cysteine on CdS quantum dots (QDs), but the spherical shape prevents an efficient chirality imprinting, limiting the dissymmetry factor (g-factor) to the order of  $3 \times 10^{-4}$  with this ligand<sup>[2]</sup>. More recently, studies have focused on grafting cysteine ligands on CdSe nanoplatelets (NPLs), which act as quantum wells possessing a defined number of atomic monolayers and offering a finer tuneable emission band as well as a shape that undergoes deformation more easily<sup>[3][4]</sup>. While those studies have successfully yielded semiconducting NPLs with chiroptical properties, thicker NPLs remain an order of magnitude below their thinner counterparts, but possess the best emission properties. Our work shows that it is possible to obtain higher g-factors on thicker 5ML NPLs while still partially retaining their fluorescence properties by synthesizing a series of derivatives of tartaric acid and using them as ligands with the carboxylic acid as the binding group. We first focused on optimizing the conditions under which the ligand exchange is made in order to obtain grafted NPLs with g-factors of the order of  $2.2 \times 10^{-3}$  for both 4ML and 5ML. Different alkyl chains were tested for the grafting ligands and proved that some features of the CD spectrum can be affected by the overall structure of the ligands, even the parts remote from the chiral centres. The alkyl chain also affected the colloidal stability of the grafted NPLs. Finally, we proved that our grafting protocol can be extended to 2ML and 3ML NPLs.

### References:

1. M. P. Moloney, Y.K. Gun'ko, J. M. Kelly, *Chem. Commun.*, **2007**, 38, p.3900-3902.
2. S.A. Gallagher et Al., *J. Mater. Chem.*, **2010**, 20, p.8350-8355.
3. D.A. Kurtina et Al., *Chem. Mater.*, **2019**, 31, p.9652-9663.
4. J. Hao et Al., *Adv. Optical Mater.*, **2021**, 9, 2101142.

**Acknowledgment:** Benoît Wagnon, Leonardo Curti, Benoît Fleury for contributing to the work. This work is part of a project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant agreement No.865995).

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords :** Nanostructured titania; Mixed oxides, Phase transformation; Thermal Stability, Photocatalysis

**Disciplinary fields involved:** Physical Chemistry, Materials Chemistry

**Sustainable Development Goals\* eventually involved in your research: -**

## Influence of heteroelement addition on the properties of nanostructured titania

L. Michelin<sup>1,2</sup>, B. Lebeau<sup>1,2</sup>, S. Rigolet<sup>1,2</sup>, L. Josien<sup>1,2</sup>, L. Vidal<sup>1,2</sup>, F. Jonas<sup>3</sup>, J.L. Blin<sup>3</sup>

1. IS2M UMR 7361, Université de Haute Alsace (UHA), CNRS, F-68100 Mulhouse, France
2. Université de Strasbourg, 67000 Strasbourg, France
3. L2CM ; Université de Lorraine, CNRS, F-54000 Nancy, France

Titanium dioxide is widely used in the formulation of sunscreen and plastics, as pigments or in catalysis<sup>1</sup>. It is also a semiconductor widely considered for its photocatalytic properties<sup>2</sup>. Depending on the targeted application, one of the crystallographic forms of titania should be favored during the titania preparation. Thus, up to now many efforts are devoted to control the crystallization of TiO<sub>2</sub> and to tune the anatase to rutile phase transition. Moreover, the applications of titania in photocatalysis and in catalysis show the interest to prepare TiO<sub>2</sub> with high specific surface area and thermal stability. To increase the specific surface area one way consists in the extension of the surfactant templating process<sup>3</sup>, reported for the preparation of ordered silica mesoporous materials. However, in most cases the mesostructures collapse and loose most of the porosity after being heating at 300-350 °C because of the intrinsical crystallization of anatase<sup>4</sup>. To overcome this drawback (nano)composites or mixed oxides can be formed by the introduction of heteroelement, during the preparation of the mesostructured titania. Here, we have shown that thanks to the protector role played by the amorphous SiO<sub>2</sub> surrounded the titania crystallites and by comparison with the bare mesostructured titania the crystallization is delayed and the growth of the anatase particles is limited due to the « glass » effect<sup>5</sup>. The transformation from anatase to rutile also occurs at higher temperature. As a consequence, the photodegradation rate of methyl orange under UV light is inhibited.

### References:

1. O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, Prog. Solid State Chem. 32 (2004) 33-177.
2. M. Fox, M. Dulay, Heterogeneous Photocatalysis, Chem. Rev., 1993, 93, 341-357.
3. K. Zimny, T. Roques-Carnes, C. Carteret, M.J. Stébé, J.L. Blin, J. Phys. Chem. C, 2012, 116, 6585-6594.
4. S.Y. Choi, M. Mamak, N. Coombs, N. Chopra, G.A. Ozin, Adv. Funct. Mater., 2004, 14, 355-344.
5. F. Jonas, B. Lebeau, L. Michelin, C. Carteret, L. Josien, L. Vidal, S. Rigolet, P. Gaudin, J.L. Blin, Microporous Mesoporous Mater., 2021, 315, 110896.

### Acknowledgment:

We would like to thank the platform "Spectroscopies et Microscopies des Interfaces" from LCPME. The platforms "X-ray Diffraction, FTIR and Raman spectroscopy, Electronic Microscopy, NMR" of IS2M are also acknowledged. Florian Jonas thanks the « Region Grand-Est » for the financial support of his PhD.



**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

## Innovation for resolute measurement of nanocarriers and bioconjugates in native state

Cédric Sarazin<sup>1</sup>, Mathilde Lelan<sup>1</sup>, Giovanni Brambilla<sup>2</sup>, Gérard Meunier<sup>1,2</sup>

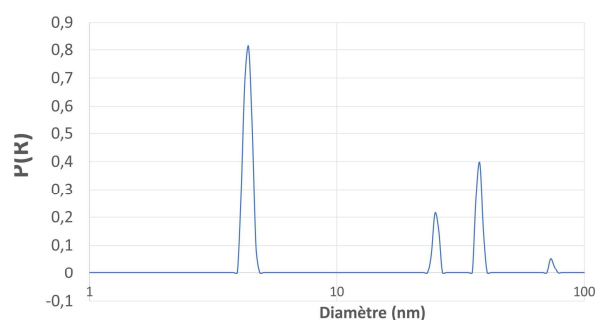
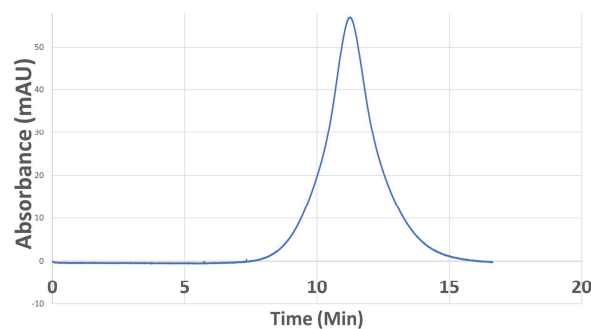
<sup>1</sup>Nanoscale Metrix, Toulouse, France

<sup>2</sup> Formulaction, Toulouse, France

**Contact:** [cedric.sarazin@formulaction.com](mailto:cedric.sarazin@formulaction.com)

### Abstract

The assessment of the absolute size of mixture of nano-objects is a challenge in biophysical characterization. There are a limited number of affordable technologies that provide accurate particles size distribution down to 0.5nm. Current technics such as DLS, A4F/SEC-MALS, NTA are often not suitable to work in native form. Indeed, denaturation occur during sample preparation or analysis: filtration, dilution or shear stress.



The innovation is either label free or labelled for more specificity, with no need for calibration and no matrix effects. Tolerant to salts, excipients and aggregates it is now possible to get a full native characterization of several pharmaceutical products such as LNP, exosomes, antibodies, or metallic nanoparticles.

The Taylorgram and the size distribution presented hereafter illustrates as a model, the powerful of the technology on a mixture containing four polystyrenesulfonate sodium salts.



**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Inorganic nanoparticles, lanthanides, microflows

**Disciplinary fields involved:** Chemistry, Physics, Mechanics

**Sustainable Development Goals\* eventually involved in your research:** Affordable and Clean Energy (Goal 7), Climate Action (Goal 13)

## LaPO<sub>4</sub>:Eu nanorods as polarized luminescence emitters and their application for *in situ* flow shear monitoring in an energy harvesting device.

Lilian Magermans<sup>1</sup>, Jeongmo Kim<sup>1</sup>, Zijun Wang<sup>1</sup>, Thierry Gacoin<sup>1\*</sup>, Jongwook Kim<sup>1\*</sup>

1. *Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, CNRS, Ecole Polytechnique, IP-Paris, Palaiseau, France*

Luminescent nanoparticles play a crucial role as signaling probes when observing micro- and nanoscale objects and phenomena. Considering lanthanides as a luminescence activators is highly appealing due to their high quantum yield and sharp emission peaks. Moreover, when doped in a non-cubic monocrystal, their emission becomes polarized as f-f transitions are only allowed in particular crystallographic directions independent on particle size or morphology.

In this work, we synthesize monocrystalline LaPO<sub>4</sub>:Eu nanorods as polarized luminescence emitters. LaPO<sub>4</sub> provides an excellent host for lanthanides and can be synthesized through common hydrothermal synthesis into colloidal suspensions with remarkable stability [1]. The obtained nanorods have a large aspect ratio which allows for their efficient collective alignment under external forces such as electric fields or flow shear. Upon doping with Eu<sup>3+</sup> the nanorods exhibit strongly polarized luminescence due to their anisotropic crystal structure. Our group has demonstrated the possibility to determine the three-dimensional orientation of single rods by comparing spectroscopic measurements to emission spectra collected from highly aligned assemblies of nanorods [2]. This spectroscopy-based orientation analysis can furthermore be used to characterize microfluidic flows, as the collective orientation of nanorods is directly related to flow conditions they are subjected to [3]. These photoluminescent LaPO<sub>4</sub>:Eu nanorods therefor provide a powerful tool for *in situ* shear flow monitoring, which we explore for the characterization of energy harvesting in microfluidic channels.

### References:

- [1] Wang Z., Kim J., Magermans L., Corbella F., Florea I., Larquet E., Kim J., Gacoin T, *Nanoscale* 13, no. 40 (2021): 16968–76
- [2] Kim J., Chacón R., Wang Z., Larquet C., Lahlil K., Leray A., Colas-des-Francis G., Kim J., Gacoin T., *Nature Communications* 12, no. 1 (2021): 1943.
- [3] Kim J., Michelin S., Hilbers M., Martinelli L., Chaudan E., Amselem G., Fradet E., et al. *Nature Nanotechnology* 12, no. 9 (2017): 914–19.

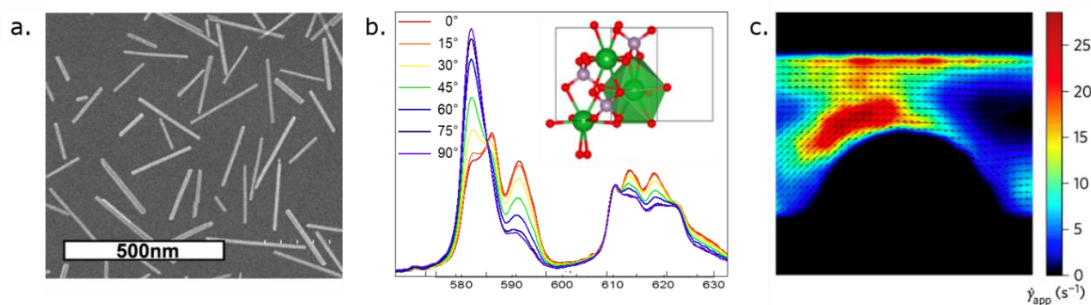


Figure 1. (a) SEM image of a typical sample of LaPO<sub>4</sub>:Eu nanorods (b), polarized luminescence of an aligned array of rods – inset : lattice site of the Eu<sup>3+</sup> ion (c), flow shear tomography image of a microfluidic channel with a constriction.

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Silver Sulfide, Soft chemistry synthesis, Nanothermometry, Luminescence quenching, reactivity with hydrogen peroxide

**Disciplinary fields involved:** Chemistry, Nanophotonics

**Sustainable Development Goals\* eventually involved in your research:** Good Health and well being (Goal 3), Responsible Consumption & Production (Goal 12)

## Luminescence impact on green silver sulfide (Ag<sub>2</sub>S) nanothermometer with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

Thomas Naillon<sup>1,2</sup>, Bruno Viana<sup>2</sup>, Lise Abiven<sup>3</sup>, Mahshid Hashemkhani<sup>3</sup>, Florence Gazeau<sup>3</sup>, Corinne Chanéac<sup>1</sup>

1. LCMCP, UMR7574 CNRS, Sorbonne Université, 4 Place Jussieu, 75005 Paris, France
2. IRCP, UMR8247 CNRS, PSL Chimie ParisTech, 11 Rue Pierre et Marie Curie, 75005 Paris, France
3. MSC, UMR7075 CNRS, Université Paris Cité, 45 rue des Saints Pères, 75006 Paris, France

Temperature is one of the most common physical quantities and contributes greatly to mechanical strength, chemical reactivity and biological processes. Luminescence nanothermometry is related to temperature measurements at the nanometric scale with high spatial and temporal resolution using nanoparticles for which an extinction of luminescence is observed during a rise of temperature (*Figure 1*)<sup>1</sup>. Nanothermometry has many applications since it reflects physical, chemical or biological phenomena. For example, in medicine, the measurement of nanothermometry would allow earlier diagnosis of certain diseases. In this field, silver sulfide (Ag<sub>2</sub>S) has demonstrated its effectiveness and low toxicity. They are able to be excited in the first window of transparency of biological tissues (NIR-I) and to emit radiation in the second window (NIR-II). The decrease of the luminescence with heating allows to calibrate the temperature probe with a very good sensitivity and this effect has been shown for different ligands<sup>2</sup>. Nevertheless, a great work of optimization must be put in place to understand and make this material more efficient. The luminescence of nanoparticles is directly impacted by the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)<sup>3</sup>, which is one of the species produced by the reactive oxygen species (ROS) during the inflammatory response. This impact is characterized by an increase or a decrease in the luminescence (*Figure 2*). It was shown with several coatings of Ag<sub>2</sub>S which was possible to have very different responses to H<sub>2</sub>O<sub>2</sub>. It would seem that the presence of H<sub>2</sub>O<sub>2</sub> around the Ag<sub>2</sub>S would cause reactions on the surface of the metallic core, which would justify the different behaviours depending on the coating.

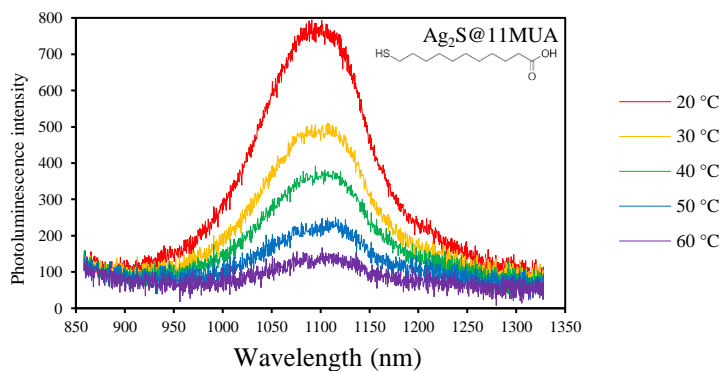


Figure 1: Evolution of the photoluminescence (PL) for temperature increase on Ag<sub>2</sub>S nanoparticles coating with 11-MercaptoUndecanoic Acid (11MUA).

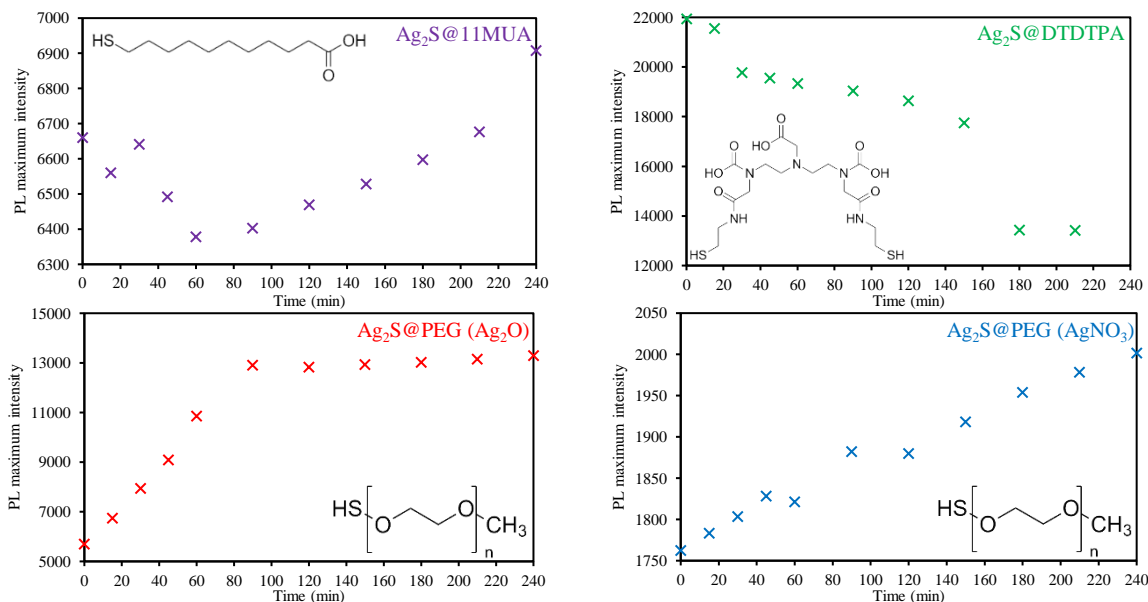


Figure 2: Impact of H<sub>2</sub>O<sub>2</sub> on the photoluminescence (PL) maximum pic of Ag<sub>2</sub>S nanoparticles coating with different ligands during 4h after addition of H<sub>2</sub>O<sub>2</sub> at constant temperature.

## References:

- Paściak, A.; Marin, R.; Abiven, L.; Pilch-Wróbel, A.; Misiak, M.; Xu, W.; Prorok, K.; Bezkrvnyi, O.; Marciniak, Ł.; Chanéac, C.; Gazeau, F.; Bazzi, R.; Roux, S.; Viana, B.; Lehto, V.-P.; Jaque, D.; Bednarkiewicz, A. Quantitative Comparison of the Light-to-Heat Conversion Efficiency in Nanomaterials Suitable for Photothermal Therapy. *ACS Appl. Mater. Interfaces* **2022**, *14* (29), 33555–33566. <https://doi.org/10.1021/acscami.2c08013>.
- Jaque, D.; Vetrone, F. Luminescence Nanothermometry. *Nanoscale* **2012**, *Issue 15* (4), 4301–4326. <https://doi.org/10.1039/C2NR30764B>.
- Zhang, X.; Wang, W.; Su, L.; Ge, X.; Ye, J.; Zhao, C.; He, Y.; Yang, H.; Song, J.; Duan, H. Plasmonic-Fluorescent Janus Ag/Ag<sub>2</sub>S Nanoparticles for *In Situ* H<sub>2</sub>O<sub>2</sub>-Activated NIR-II Fluorescence Imaging. *Nano Lett.* **2021**, *21* (6), 2625–2633. <https://doi.org/10.1021/acs.nanolett.1c00197>.



**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Zeolite-Templated Carbons, microporous carbons, ordered carbons

**Disciplinary fields involved:** Materials chemistry, Chemical engineering

**Sustainable Development Goals\* eventually involved in your research:** -

## Micropore 3D graphenes: circumventing essential issues in large scale synthesis

S. Compère<sup>1</sup>, T. Aumond<sup>1</sup>, L. Perrier<sup>2</sup>, I. Batonneau-Gener<sup>1</sup>, A. Sachse<sup>1</sup>

1. IC2MP, groupe SAMCAT, Université de Poitiers, Poitiers, France
2. LFCR, groupe G2MP, Université de Pau et des pays de l'Adour, Pau, France

Micropore 3D graphenes also known as Zeolite-Templated Carbons (ZTC) are highly microporous and nanostructured materials that feature unparalleled electrical conductivity and surface area [1]. As a result, they are excellent candidates for the development of catalysts in fuel cells and as adsorbents in gas storage such as methane and hydrogen at cryogenic and room temperature. One key barrier that needs to be lifted in order to allow for their large-scale synthesis and hence their commercialization is the generation of low-quality ZTC when attempting to synthesize greater quantities than 1 g. ZTC are achieved through the use of a zeolite as sacrificial template and a gaseous carbon source classically using static reactors. This has the inconvenience of the development of preferential pathways during synthesis, inducing very heterogeneous distribution of gases in the reactor and leading hence to unequal zeolite filling. To remedy this inconvenience, we propose the design of a rotary reactor, which allows for homogeneous filling of zeolites on the kg scale, and hence to achieve large-scale synthesis of high quality ZTC.

[1] H. Nishihara, T. Kyotani, *Chem. Commun.*, 54, 5648 (2018)



**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** nanoparticules, molten salt, boron phosphide, photocatalysis

**Disciplinary fields involved:** Solid-state Chemistry, material science

**Sustainable Development Goals\* eventually involved in your research: -**

## New boron phosphide nanocrystals synthesized in molten salt

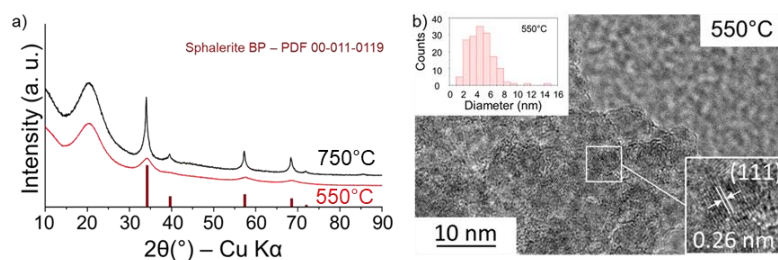
**A. Séné<sup>1</sup>, F. Igoa<sup>1</sup>, C. Coelho-Diogo<sup>1</sup>, C. Gervais<sup>1</sup>, A. Miche<sup>2</sup>, S. Casale<sup>2</sup>, D. Portehault<sup>1</sup>**

1. *Laboratoire de chimie de la matière condensée de Paris, Sorbonne Université, CNRS, Paris, France*
2. *Laboratoire de réactivité de surface, Sorbonne Université, Paris, France*

Boron phosphides exhibit exciting properties, from hardness to semi-conductor behaviour, thermoelectricity and photocatalysis. Cubic boron phosphide (*c*-BP) is especially a good candidate for photocatalytic water splitting [1,2] and CO<sub>2</sub> reduction [3].

The synthesis of nanostructured cubic boron phosphide (*c*-BP) is a challenge due to the high energetic cost required to order the framework of covalent bonds into the zinc-blende structure. *c*-BP can be synthesized by various ways, including high temperature solid-state reaction from the elements, synthesis in tin flux, high pressure synthesis to only quote a few [1]. These approaches yield single crystals, films or amorphous nanoparticles. Nowadays, only one synthesis is reported to deliver *c*-BP nanoparticles by a top-down approach, which offers a poor control of the size and of the crystallinity of the particles [4].

Our team has developed a new bottom-up synthesis of *c*-BP crystalline nanoparticles with diameter below 5 nm, thus delivering a new nanomaterial with high surface area. Our approach relies on molten salts media [5] to fasten reactions, even below the temperatures usually employed to reach this compound. We will discuss in detail the structural and morphological features of this nanomaterial *via* numerous characterisations that allow us to have a better understanding of the structure and composition of the material. In addition, we will show the preliminary results on their catalytic properties for water splitting.



**Figure 1.** a) Powder XRD pattern of *c*-BP particles synthesized b) TEM images of *c*-BP particles with distribution size insert

### References:

- [1] K. Woo, et al. *Mater. Res. Express.* 7(2016)
- [2] L. Shi, et al. *Nano Energy.* 28, 158 (2016)
- [3] S. Mou, et al. *Adv. Mater.* 31 (2019)
- [4] H. Sugimoto, et al. *RCS Advances.* 11, 8427 (2015)
- [5] D. Portehault, et al. *Chem. Soc. Rev.* 51, 4828 (2022)

**Aknowledgments:** ERC GENESIS, LCMCP

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Hollow Au Nanoparticles, Localized Surface Plasmon Resonance, Biosensor.

**Disciplinary field involved:** Chemistry

**Sustainable Development Goals\* eventually involved in your research:** Life and Land (Goal 15)

## Optimization of a LSPR Sensor Chip Using Hollow Au Nanoparticles

Daoming Sun<sup>1,2</sup>, Michèle Salmain<sup>2,\*</sup>, Souhir Boujday<sup>1,\*</sup>

1. *Laboratoire de Réactivité de Surface (LRS). Sorbonne Université. CNRS. Paris. France.*

2. *Institut Parisien de Chimie Moléculaire (IPCM). Sorbonne Université. CNRS. Paris. France.*

Au nanostructures currently arouse an extensive interest in biological and chemical sensing<sup>1,2</sup> due to their sensitive optical response to slight changes in the refractive index (RI) of the dielectric environment. This work illustrates the optimization of a localized surface plasmon resonance (LSPR) sensor chip using hollow Au nanoparticles (HAuNPs), which could be utilized for sensitive biosensing. A bottom-up approach was applied, considering its convenience and cheapness. We started with the chemical synthesis of colloidal HAuNPs having varying sizes (20–100 nm) and shell thicknesses (0.2–0.4 x radius). The refractive index sensitivity (RIS) of the resulting HAuNPs was measured in solution so as to optimize the sensing performance of the sensor chip. Then the optimal HAuNP sample was immobilized on APTES-treated glass slides. Experimental parameters of glass functionalization and colloid immobilization were optimized to obtain a sensor chip showing an intense LSPR band and well dispersed HAuNPs on the surface. As a comparison, another sensor chip using solid Au nanoparticles (AuNPs) with a similar size was prepared. The RIS of these two LSPR sensor chips was measured. It is found that the RIS of immobilized HAuNPs is 2.4 times that of AuNPs. Furthermore, no obvious decline of RIS was observed after immobilization of HAuNPs on the glass surface. This is an advantage over anisotropic nanoparticles, whose RIS will decrease after immobilization on a planar surface<sup>3</sup>. In summary, HAuNPs show high and stable RIS, which makes them favorable for substrate-based LSPR biosensors.

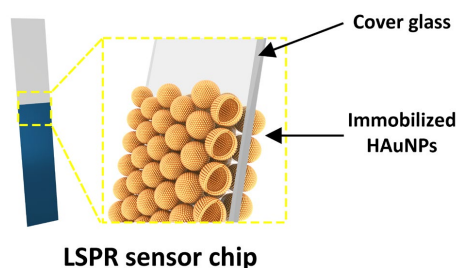


Figure 1. Scheme of a LSPR sensor chip using cover glass and HAuNPs.

## References:

- (1) Li, Y.; Schluesener, H. J.; Xu, S. Gold nanoparticle-based biosensors. *Gold Bulletin* 2010, 43 (1), 29-41. DOI: 10.1007/BF03214964.
- (2) Zhang, L.; Mazouzi, Y.; Salmain, M.; Liedberg, B.; Boujday, S. Antibody-Gold Nanoparticle Bioconjugates for Biosensors: Synthesis, Characterization and Selected Applications. *Biosensors and Bioelectronics* 2020, 165, 112370. DOI: 10.1016/j.bios.2020.112370.
- (3) Hegde, H. R.; Chidangil, S.; Sinha, R. K. Refractive index sensitivity of Au nanostructures in solution and on the substrate. *Journal of Materials Science: Materials in Electronics* 2022, 33 (7), 4011-4024. D

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Polarized luminescence, lanthanide, LaPO<sub>4</sub>, microfluidics

**Disciplinary fields involved:** Chemistry and Physics

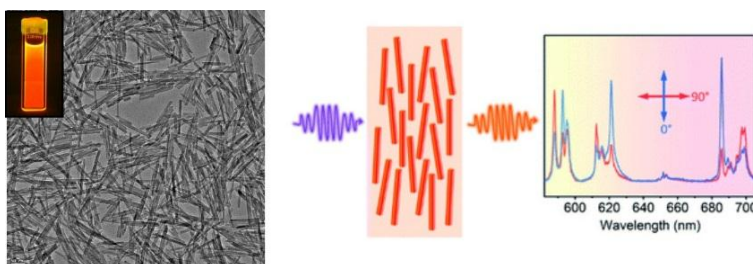
## Optimization of anisotropic LaPO<sub>4</sub>:Eu<sup>3+</sup> nanorods as polarized luminescence probes in fluid flow

Qilin Zou<sup>1</sup>, Zijun Wang<sup>1</sup>, Zhengyu Zhang<sup>1</sup>, Lilian Magermans<sup>1</sup>, Jongwook Kim<sup>1,\*</sup> and Thierry Gacoin<sup>1,\*</sup>

1. *Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, CNRS, IP Paris, 91128 Palaiseau, France*

Polarized luminescence in anisotropic particles is highly appealing for the optical monitoring of the particle orientation induced by external stimuli such as electric or magnetic fields, and fluid flow.<sup>1</sup> For such applications, Eu<sup>3+</sup> doped LaPO<sub>4</sub> nanorods appear as excellent candidates as they present unique luminescence polarization features originating from f electrons transitions from Eu<sup>3+</sup> interestingly modulated by the anisotropic symmetry of host crystal structure. First results have been demonstrated for orientation analysis in microfluidic channels<sup>2</sup> and further improvements of the technique are linked to the development of more performant nanorods. Researches on that topic focus on i) improved brightness and DOP (degree of polarization) of the emission, ii) appropriate dispersion of the rods in the host media of interest and iii) adjusting the particles shape (mainly aspect ratio) in order to get the optimal sensitivity of the orientation measurement for the range of intensity of the stimuli leading to orientation.

Recently, we have explored a microwave heating strategy<sup>3</sup> for the synthesis of monazite LaPO<sub>4</sub> nanorods with high luminescence efficiency and excellent colloidal stability as attested by liquid crystalline behaviors, as well as variable aspect ratios by adding surfactant. Furthermore, high DOPs are observed for both the forced electric dipole and the magnetic dipole transitions of Eu<sup>3+</sup> emission in polarization measurements. By virtue of a facile surface functionalization with selected zwitterionic polymers, the nanorods can be further stabilized in saline biofluids. These results have shown that the nanorods are outstanding candidates used as probes for 3D tomography of flow shear stress in microfluidics.



## References:

1. Kim, J.; De la Cotte, A.; Deloncle, R.; Archambeau, S.; Biver, C.; Cano, J.-P.; Lahlil, K.; Boilot, J.-P.; Grelet, E.; Gacoin, T., Lapo4 Mineral Liquid Crystalline Suspensions with Outstanding Colloidal Stability for Electro-Optical Applications. *Adv. Funct. Mater.* **2012**, *22*, 4949-4956.
2. Kim, J.; Michelin, S.; Hilbers, M.; Martinelli, L.; Chaudan, E.; Amselem, G.; Fradet, E.; Boilot, J.-P.; Brouwer, A. M.; Baroud, C. N.; Peretti, J.; Gacoin, T., Monitoring the Orientation of Rare-Earth-Doped Nanorods for Flow Shear Tomography. *Nat. Nanotechnol.* **2017**, *12*, 914-919.
3. Wang, Z.; Kim, J.; Magermans, L.; Corbella, F.; Florea, I.; Larquet, E.; Kim, J.; Gacoin, T., Monazite Lapo4:Eu<sup>3+</sup> Nanorods as Strongly Polarized Nano-Emitters. *Nanoscale* **2021**, *13*, 16968-16976.



**Thematic Session:** Nanochemistry, nanoparticles, nanocatalysis **Keywords:** Hybrid imogolites, cement matrix,  $C_3S$ , structure interactions

**Disciplinary fields involved:** Physics, inorganic materials, chemistry Sustainable Development

**Goals\* eventually involved in your research:** -

## Chemical reactivities between hybrid imogolites and a cementitious phase: formulation of a conditioning matrix for nuclear waste stabilization

Puel E<sup>1</sup>., Testard F<sup>1</sup>., Poulesquen A<sup>2</sup>., Cau Dit Coumes C<sup>2</sup>., Thill A<sup>1</sup>.

1. LIONS, NIMBE, CEA Saclay, Université Paris-Saclay, 91191 Gif-Sur-Yvette, France
2. LCBC, SEAD, CEA Marcoule, Université Montpellier, 30207 Bagnols-Sur-Cèze, France

In the context of conditioning non-incinerable radioactive oil by using Janus particles to encapsulate oil in cement, we will focus on the impact of hybrid imogolites in the cement formulation with respect to Portland cement hydration. Janus particles are hybrid nano-clays (aluminosilicate imogolites) with tubular shape<sup>1</sup>. Their character come from specific properties: internal surfaces being covered by Si-CH<sub>3</sub> groups can stabilize hydrophobic compounds. External surfaces formed by alumina is hydrophilic and positively charged up to pH~10. It has affinity for the mixing water used for cement hydration. Hexadecane was used as a non-radioactive surrogate of the contaminated oil. Hydration of cement pastes with variable contents of imogolites was monitored using isothermal microcalorimetry. Unlike hexadecane, hybrid imogolites were shown to retard the hydration process. To understand the mechanism involved in this delay, a simplified system, consisting in hybrid imogolites and tricalcium silicate( $3CaO.SiO_2$ )(main Portland constituent), was investigated. Hydration of tricalcium silicate after increasing periods of time was characterized by solid state NMR, XRD and TGA. Imogolites were progressively destabilized under the alkaline conditions set by the cement paste, releasing aluminate ions to the solution, which were consumed to precipitate an aluminum-substituted calcium silicate hydrate (referred as C-A-S-H). This precipitation could be responsible for the delay in cement hydration, since it is known that C-A-S-H particles do not act as nucleation and growth sites for further calcium silicate hydrate (C-S-H)<sup>2</sup>. Role of C-A-S-H phase for the affinity with oil of the hydrated hybrid cement paste is still to be explored.

### References:

1. P.D.G. Cradwick, V.C. Farmer, J.D. Russell, et al. Imogolite, a Hydrated Aluminium Silicate of Tubular Structure. *Nature Physical Science* **1972**, 240 (104), 187–189.
2. F. Begarin, S. Garrault, A. Nonat, L. Nicoleau. Hydration of alite containing aluminium. *Advances in Applied Ceramics* **2011**, 110 (3), 127–130.

**Aknowledgments:** The authors gratefully acknowledge the French Alternative Energies and Atomic Energy Commission (CEA) and the FOCUS research program for funding.

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords** (max. 4-5): carbon electrodes; electrochemistry; CO<sub>2</sub> conversion; N<sub>2</sub> reduction.

**Disciplinary fields involved:** Chemistry, Physics

**Sustainable Development Goals\* eventually involved in your research:** Affordable & Clean Energy (Goal 7), Good Health and Well-being (Goal 3)

## Screening of nanoporous carbon electrodes for the electrochemical conversion of CO<sub>2</sub> and N-compounds

Ali FAYAD<sup>1</sup>, Elhassan AMATER<sup>1</sup>, Jesus INIESTA<sup>2</sup>, Conchi ANIA<sup>1</sup>

1. CEMHTI, CNRS (UPR 3079), Université d'Orléans, 45071 Orléans, France

2. Instituto Universitario de Electroquímica, Universidad de Alicante, 03080 Alicante, Spain

The seek of sustainable technological solutions for the production of ammonia (a promising hydrogen vector) and urea (most widely used fertilizer) have recently received the attention due their outstanding market and economical role in our society. Today, NH<sub>3</sub> (Haber-Bosch) and urea (Bosh Meiser) are the produced in high energy consuming processes at extreme *T* and *P* conditions. Their electrochemical production is an interesting alternative, as it would allow the direct utilization of renewable energy and milder conditions [1]. The challenge is to find efficient and abundant catalysts for reaching high conversions and suppressing side reactions (e.g., hydrogen evolution). In this regard, metal-free carbon-based catalysts are excellent candidates due to their versatility of structure, abundance and conductivity [2]. The aim of this study is to screen the electrochemical activity of a pool of carbon materials for the electrochemical conversion of CO<sub>2</sub> and N-compounds (nitrogen, nitrates) into added value chemicals and fuels. Carbon electrodes have been prepared and characterized (by linear sweep, cyclic voltammetry, electrochemical impedance spectroscopy) to obtain a better understanding about the charge transfer ability in the CO<sub>2</sub> and N- electrocatalytic reactions. Data obtained has revealed a good performance for the electrochemical conversion of CO<sub>2</sub> to CO at low overpotentials. The selectivity towards the reduction of CO<sub>2</sub> over the hydrogen evolution reaction seems to be governed by the structural defects of the electrodes. Furthermore, the electroreduction of nitrate is discussed in terms of the physicochemical properties of the studied carbons, to get high ammonia production rates and faradaic efficiencies.

### References:

[1] Chen, He, et al. *Small Science* 1 (2021) 2100070; Li, Li, et al. *Catal Today* 12 (2022) 388.

[2] Wang, Hong, et al. *Angewandte Chemie* 129 (2017): 7955; Yao, Pengfei, et al. *ACS Sustainable Chemistry & Engineering* 7 (2019): 5249; Li, Xiao et al, *Mat. Today Phys*, 19 (2021) 100431.

Acknowledgments: The financial support from Region Centre Val de Loire (grant MATHYFON) is acknowledged. A. Fayad thanks Université d'Orléans for a PhD fellowship.

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** transition aluminas, oxide nanoparticles, vibrational spectroscopy, structural disorder

**Disciplinary fields involved:** Chemistry, Physics, Spectroscopy

**Sustainable Development Goals eventually involved in your research:** Responsible Consumption & Production (Goal 12), Climate Action (Goal 13)

## Structural disorder and vibrational properties of transition aluminas

Iñigo González de Arrieta<sup>1,2</sup>, Abdelali Zaki<sup>1</sup>, Aurélien Canizarès<sup>1</sup>, Emmanuel Véron<sup>1</sup>, Cécile Genevois<sup>1</sup>,  
Leire del Campo<sup>1</sup>, Cédric Blanchard<sup>1</sup>, Olivier Rozenbaum<sup>1</sup>

1. CNRS, CEMHTI UPR3079, Univ. Orléans, F-45071 Orléans, France

2. Physics Department, University of the Basque Country (UPV/EHU), E-48940 Leioa, Spain

Transition aluminas, obtained by thermal decomposition of the mineral boehmite, are essential for catalytic applications due to their large surface areas and amphoteric nature. Three phases can be singled out in the so-called metastable cascade ( $\gamma \rightarrow \delta \rightarrow \theta \rightarrow$  stable  $\alpha\text{-Al}_2\text{O}_3$ ), with the structures of the first two being controversial and heavily dependent on the synthesis procedure [1]. In this work, we present infrared and Raman spectroscopic results on  $\gamma$  and  $\delta$  alumina nanopowders. Their vibrational spectra can be quantitatively interpreted and related to their crystal structure, although signs of structural disorder and features not predicted by group theory are observed. Both phases show very similar infrared dielectric functions, but with clear instances of mode-splitting in the  $\delta$  phase, which are related to ordering in the tetrahedral Al positions [2]. Raman spectroscopy is unable to resolve any modes corresponding to the  $\gamma$  phase, but the full lattice vibrational region is accessible for the  $\delta$  sample under UV and red laser excitations. Raman spectra are more complex than those obtained by IR spectroscopy and cannot be completely explained by factor group analysis, in the absence of dedicated theoretical studies. These results prove that vibrational spectroscopies are powerful tools for quantitative analyses of these disordered nanomaterials and suggest the need for more theoretical work to understand their properties.

### References:

[1] G. Busca, Catal. Today 226 (2014) 2–13.

[2] Y. Repelin, E. Husson, Mater. Res. Bull. 25 (1990) 611–621.

**Acknowledgment:** Iñigo González de Arrieta thanks the Basque Government for its support through a post-doctoral grant (POS-2021-2-0022).



**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** catalysis, gold nanoparticles, single molecule detection, surface-enhanced Raman spectroscopy (SERS), *in situ* spectroscopy

**Disciplinary fields involved:** chemistry, chemical physics

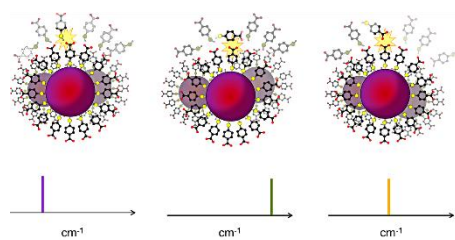
**Sustainable Development Goals\* eventually involved in your research:** None

## Studying dynamics of molecular layers covering gold nanostructures by SERS

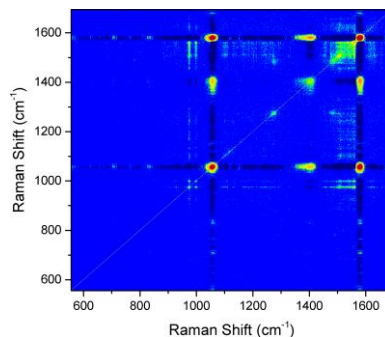
D. Oliveira de Souza<sup>1</sup>, J.-S. Girardon<sup>1</sup>, J.-F. Paul<sup>1</sup>, D. J. Hoffmann<sup>2</sup> and Elise Berrier<sup>1</sup>

1. Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 UCCS Unité de Catalyse et Chimie du Solide, Lille, France
2. Electrical Engineering Department, Federal University of Espírito Santo (UFES), Vitória-ES, Brazil

Surface-Enhanced Raman Spectroscopy (SERS) can produce a localized -and dramatic- increase of the Raman scattering by molecules adsorbed at plasmonic nanostructures. This practically allows the fast acquisition of high-quality spectral datasets over trace-level amounts and, in most favorable cases, can even detect single molecules. Motivated by such exciting promises and the prospect to investigate



reaction intermediates at single-molecule scale, we present here our study of the dynamics of adsorbed molecules over gold nanoparticles (AuNPs). To this end, we have analyzed the fluctuations of the SERS spectra over time, arising from the molecular layer covering the AuNPs. Two systems have been explored using this approach: (i) the capping layer of citrate, used to stabilize the gold nanoparticles in the Turkevich procedure<sup>1</sup> and (ii) the evolutions of p-mercaptobenzoic (p-MBA) molecules chemisorbed at AuNPs<sup>2</sup>. Such fluctuations have been refined by the means of an original set of statistic tools. This made it possible to observe, besides the follow-up of chemical evolutions, accidental transient spectral signatures, which turned out to occur randomly in time. Nevertheless, the spectral region affected by such events makes a comb of well-defined vibrational frequencies, which can be seen as individual channels which gates open at time. The mechanisms involved in the switching from an “closed” to an “open” state within a time scale of the second were proposed to arise from the formation of transient resonant structures allowing the detection of the second layer of adsorbed molecules<sup>2,3</sup>.



### References:

1. J. Turkevich, P. C. Stevenson and J. Hillier **1953** *J. Phys. Chem.* 57(7), 670-673.
2. G. Smith, J.-S. Girardon, J.-F. Paul, and E. Berrier **2016** *Phys. Chem. Chem. Phys.* 18(29), 19567-19573.
3. D. Oliveira de Souza, J.-S. Girardon, D. J. Hoffmann† and E. Berrier **submitted**.

**Thematic Session :** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Magnetic Nanoparticles, synthesis, functionalization, coating, magnetocuring

**Disciplinary field involved:** Chemistry

**Sustainable Development Goals\* eventually involved in your research:** Affordable and clean energy (Goal 7), Industry innovation and infrastructure (Goal 9)

## Synthesis and Colloidal Stabilization of Manganese and Zinc Ferrite Magnetic Nanoparticles for failsafe Magnetocuring of resins

Naoures HMILI<sup>1</sup>, Ferdaous BEN ROMDHANE<sup>1</sup>, Sophie NEVEU<sup>3</sup>, Tran QUANG DUNG<sup>2</sup>, Raju. V. RAMANUJAN<sup>2</sup>, Terry STEELE<sup>2</sup>, Souhir BOUJDAY<sup>1</sup>, Juliette BLANCHARD<sup>1</sup>.

1. *Laboratoire de Réactivité de Surface, Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique : UMR7197, Paris,*
2. *School of Materials Science and Engineering (MSE), Division of Materials Technology, Nanyang Technological University (NTU), Singapore639798, Singapore*
3. *Physicochimie des Electrolytes et Nanosystèmes Interfaciaux, Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique : UMR8234, Paris,*

Adhesive Technology is attracting increasing interest from researchers for a range of emerging applications in sports, medicine, and industry. Traditionally, one-component adhesives are designed to cure using moisture, heat, or light. However, these methods are challenging to control and implement industrially. Herein, an approach to cure adhesives remotely is of high relevance.

Our approach is based on Magnetocuring, where Magnetic Nanoparticles (MNPs) are introduced into adhesives and exposed to an Alternating Magnetic Field (AMF). Under AMF, the heat generated by MNP triggers the polymerization and curing of the adhesives (ex. Epoxy resin) (fig.1A) Also, self-regulating heating can be achieved by adjusting the Curie temperature ( $T_c$ ), i.e. Temperature above which the material loses its permanent magnetization, of the MNPs.

In this project, we synthesized a library of ferrite NPs ( $M_nxZn_{1-x}Fe_2O_4$ ) of various sizes (8 nm – 20 nm) and compositions ( $x = 0.5 - 0.9$ ) [1], [2] which were characterized by TEM, XRD and EDX. Some of us have established that this library of MNPs offers a range of  $T_c$  and Specific Absorption Rate (SAR, i.e., their heating ability) suitable for magnetocuring of adhesive without overheating [2].

For magnetocuring, MNPs must be homogeneously dispersed in the resin at low concentration to preserve its mechanical properties. Therefore, we have worked on obtaining a colloidal MNPs suspensions by optimizing their stabilization with citrates (fig.1B). Currently, we work on their coating with a silica shell, which will serve as primer for further functionalization with silanes bearing different (R) groups to allow dispersion in water and/or organic liquids.



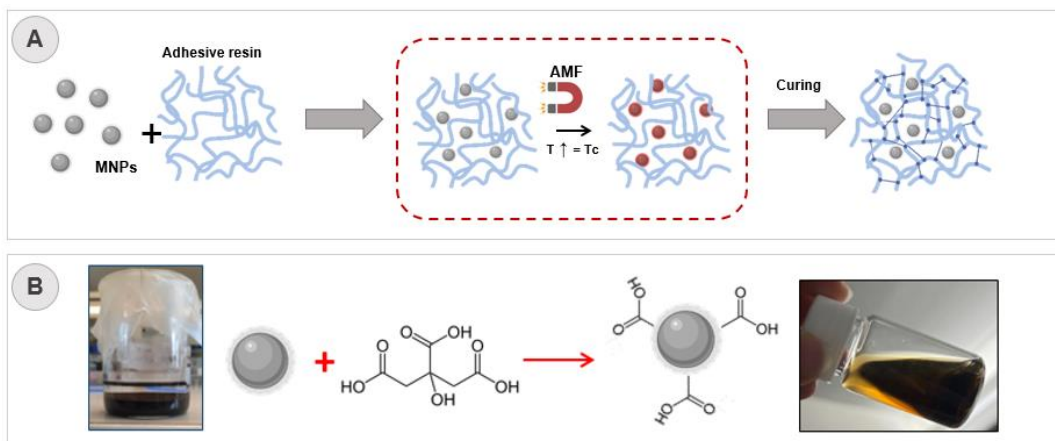


Figure 1 (A) Scheme of the magnetocuring principle (B) general scheme of citrate functionalization: visual representation of bare unstable NPs as well as colloiddally stable NPs.

## References:

- [1] P. Majewski et P. Krysiński, « Synthesis, Surface Modifications, and Size-Sorting of Mixed Nickel-Zinc Ferrite Colloidal Magnetic Nanoparticles », *Chem. - Eur. J.*, vol. 14, n<sup>o</sup> 26, p. 7961-7968, sept. 2008, doi: 10.1002/chem.200800369.
- [2] R. Chaudhary, V. Chaudhary, R. V. Ramanujan, et T. W. J. Steele, « Magnetocuring of temperature failsafe epoxy adhesives », *Appl. Mater. Today*, vol. 21, p. 100824, déc. 2020, doi: 10.1016/j.apmt.2020.100824.

## Acknowledgment:

This work is funded by SU-NTU Co-tutelle doctoral program

**Thematic Session** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Carbon Dots, Anti-counterfeiting, Security marking

**Disciplinary fields involved:** Chemistry, Physics

**Sustainable Development Goals\* eventually involved in your research:**

## Synthesis of Carbon Quantum Dots for Anti-counterfeiting

Theo Duarte<sup>1</sup>, Aurélie Broussier<sup>1</sup>, Alexandre Rabbot<sup>2</sup>, Sabine Fourier<sup>2</sup>, Anne-Laure Baudrion<sup>1</sup>, Jérôme PLAIN<sup>1</sup>, Julien PROUST<sup>1</sup>

1. *Lumière, nanomatériaux et nanotechnologie (L2n), CNRS EMR 7004 & Université de Technologie de Troyes, 12 rue Marie Curie, 10004 Troyes Cedex, France*
2. *Histoire et sources des mondes antiques - CNRS UMR 5189 – Lyon, France*

For many years, cultural property in general and archaeological artefacts have been liable to be stolen during and after the excavation process in order to be introduced to the black market. Globally, it is commonly estimated that the illicit trafficking of cultural heritage ranks among the biggest illicit trade in the world, grossing several billion dollars<sup>1</sup>.

The challenge of the project is to be able to implement a safe technical solution which makes it possible to mark archaeological artefacts in a unique way.

Carbon dots are a 0D nanomaterial made of a hybrid structure with a graphene like core of sp<sup>2</sup> carbon and an outer shell of amorphous sp<sup>3</sup> carbon. Since they are composed mainly of carbon, they constitute a safer alternative to heavy metals quantum dots and allow us to avoid trace contamination before analysis. Moreover, carbon black which is the basis of the black inks used, are chemically identical to C-dots. We integrated carbon dots synthesized using a protocol from Yan et al<sup>2</sup> into a protective coating used for marking cultural artefacts. The coating produces orange photoluminescence under UV but also green light excitation, constituting a new kind of security marking.

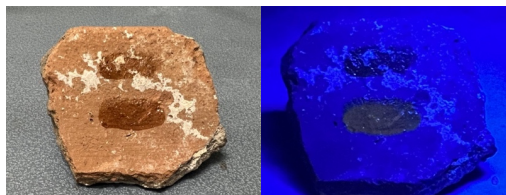


Figure: (1) carbon dots in solution under green laser excitation; (2) Clear nail polish for classic marking (top) and carbon dots incorporated to clear nail polish for marking (bottom) under visible and UV light.

### References:

- (1) Barker, A. W. Looting, the Antiquities Trade, and Competing Valuations of the Past. *Annu. Rev. Anthropol.* **2018**, 47 (1), 455–474. <https://doi.org/10.1146/annurev-anthro-102116-041320>.
- (2) Yan, F.; Zhang, H.; Yu, N.; Sun, Z.; Chen, L. Conjugate Area-Controlled Synthesis of Multiple-Color Carbon Dots and Application in Sensors and Optoelectronic Devices. *Sens. Actuators B Chem.* **2021**, 329, 129263. <https://doi.org/10.1016/j.snb.2020.129263>.

**Acknowledgments:** We thank the Laboratoire Histoire et sources des mondes antiques (HISOMA) for providing cultural artefacts for testing, the Centre de recherche de l'École National Supérieur de Police (CRENSP) for their collaboration on security matters and the Agence National de Recherche (ANR) for financing our project

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** nanoparticles, alloy, metal, synthesis, catalysis

**Disciplinary fields involved:** chemistry Sustainable

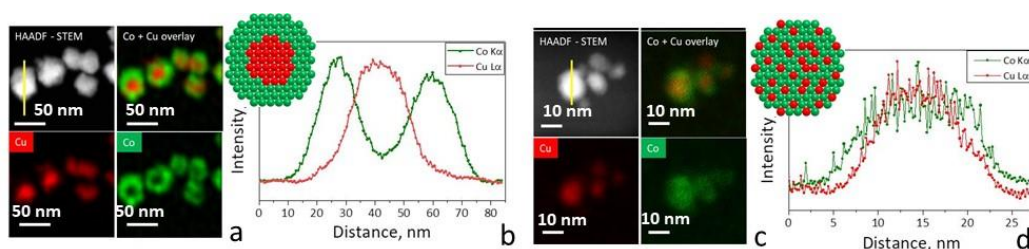
**Development Goals\* eventually involved in your research:**

## Synthesis of core-shell and nanoalloys from immiscible Cu and Co elements; application in dehydrogenation catalysis

Lorette Sicard<sup>1</sup>, Ning Huang<sup>1</sup>, Jean-Yves Piquemal<sup>1</sup>

1. ITODYS, CNRS, UMR7086, Université Paris Cité

Nanoalloys are very attractive in catalysis since they generally exhibit synergetic properties compared to monometallic nanoparticles (NPs). We recently synthesized unsupported CoRu nanoalloys and proved that they were more efficient for the acceptorless dehydrogenation of alcohols (ADA) than their Co or Ru counterparts.<sup>1</sup> Noble metal-free alloys are even more appealing.  $\text{Cu}_x\text{Co}_{100-x}$  bimetallic NPs were considered as Cu is also active for ADA<sup>2</sup> while Co, also active, permits magnetic recyclability. Nevertheless, it constitutes a real challenge as these metals are not miscible at the bulk state.<sup>3</sup> Using the polyol process,<sup>4</sup> and depending on the nature of the polyol used as a reducing agent, we obtained either Cu@Co core-shell or  $\text{Cu}_x\text{Co}_{100-x}$  alloys NPs with x ranging from 0 to 100 (Figure 1). The alloyed catalysts exhibited higher activity and selectivity for the 2-octanol dehydrogenation reaction than core-shell and pure copper and cobalt NPs. The  $\text{Cu}_{25}\text{Co}_{75}$  nano-catalyst displayed a conversion of octan-2-ol of 89 % and a selectivity towards octan-2-one of 96 % at 185°C and could be recycled ten times without a substantial loss in activity while no metal leaching could be evidenced.



**Fig. 1:** HAADF-STEM images (a. and c.) and EDX profiles (b. and d.) of  $\text{Cu}_{50}\text{Co}_{50}$  bimetallic NPs synthesized in DEG (a. and b.) and in BEG (c. and d.).

### References:

1. B. Azeredo *et al.*, *ACS Appl. Nano Mater.* **5**, 5733–5744 (2022)
2. K. Kazmierczak *et al.*, *Catal. Commun.* **148**, 106179-4937 (2021)
3. R. F. Zhang *et al.*, *Sci. Rep.*, 1–12 (2017)
4. F. Fievet *et al.*, *Chem. Soc. Rev.*, **47**, 5187-5233 (2018)

**Aknowledgments:** We acknowledge CSC for the PhD grant of N. Huang



**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** carbene ligands - gold nanoparticles - mesoionic carbenes – X-ray photoelectron spectroscopy - triazolium

**Disciplinary field involved:** Chemistry

**Sustainable Development Goals\* eventually involved in your research:** Industry, Innovation & Infrastructure (Goal 9)

## Synthesis of Mesoionic Carbene (MIC) Stabilized Gold Nanoparticles from 1,2,3-Triazolium Salts

Salem Ba Sowid<sup>1,2</sup>, Alexandre Porcheron<sup>1,2</sup>, Omar Sadek<sup>2</sup>, Nathalie Bridonneau<sup>2</sup>, Laura Hippolyte<sup>1,2</sup>, Dimitri Mercier<sup>3</sup>, Philippe Marcus<sup>3</sup>, Clément Chauvier<sup>2</sup>, Corinne Chanéac<sup>1</sup>, Louis Fensterbank<sup>2\*</sup>, François Ribot<sup>1\*</sup>

1. Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris, LCMCP, F-75005 Paris, France.
2. Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75005 Paris, France.
3. PSL Research University, Chimie Paris Tech, CNRS, Institut de Recherche de Chimie Paris, IRCP, F-75005 Paris, France.

Stabilization of gold nanoparticles (AuNPs) in colloidal suspension to ensure their functionality in various applications is a crucial challenge. Thiol-based ligands have been conventionally employed to stabilize AuNPs. However more recently, N-heterocyclic carbenes (NHCs) have gained interests as strong-binding surface ligands that can outperform thiols<sup>1,2</sup>. While classical NHCs, based on (benz)imidazole, can be modularly synthesized, time-consuming multi-step synthesis is needed to achieve unsymmetrical or functionalized NHCs. Mesoionic carbenes (MICs) on the other hand are robust subclass of NHCs. Unlike classical NHCs, MICs can be easily synthesized via simple click reaction followed by alkylation step, which gives easy access to different functions on the MIC core. Moreover, MICs are stronger  $\sigma$ -donors than the NHCs,<sup>3</sup> which should offers higher stability to the nanoparticles.

Herein, we report a one-pot straightforward synthesis of MIC-stabilized AuNPs directly from 1,2,3-triazolium salts and tetrachloroauric acid (Fig.1). Unlike previous reports<sup>4,5</sup>, our protocol does not require pre-isolation of MIC-gold complex or triazolium-gold salt. In this study, a library of MIC precursors was synthesized from which a series of stable MIC-AuNPs was isolated.

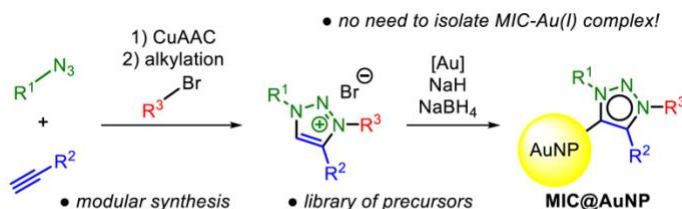


Figure 1. Scheme of the one-pot MIC@AuNPs synthesis.

The effect of nature of the MIC precursor as well as the triazolium/gold ratio were shown to have a direct effect on the size of AuNPs, demonstrated by TEM. X-ray photoelectron spectroscopy was used to characterize the nature of the nanoparticles and to confirm the presence of MICs as capping ligands on the AuNP surface. These MIC-AuNPs were demonstrated to be stable to storage in solution for months, to low/high temperatures, and to the high concentrations of exogenous thiols.

### References:

- 1- Zhukhovitskiy, A. V.; MacLeod, M. J.; Johnson, J. A. Carbene Ligands in Surface Chemistry: From Stabilization of Discrete Elemental Allotropes to Modification of Nanoscale and Bulk Substrates. *Chem. Rev.* **2015**, *115* (20), 11503–11532
- 2- Srisombat, L.; Jamison, A. C.; Lee, T. R. Stability: A Key Issue for Self-Assembled Monolayers on Gold as Thin-Film Coatings and Nanoparticle Protectants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2011**, *390* (1–3), 1–19.
- 3- Donnelly, K. F.; Petronilho, A.; Albrecht, M. Application of 1,2,3-Triazolylidenes as Versatile NHC-Type Ligands: Synthesis, Properties, and Application in Catalysis and Beyond. *Chem. Commun.* **2013**, *49* (12), 1145–1159.
- 4- Nguyen, Diep. T. H.; Bélanger-Bouliga, M.; Shultz, L. R.; Maity, A.; Jurca, T.; Nazemi, A. Robust Water-Soluble Gold Nanoparticles via Polymerized Mesoionic N-Heterocyclic Carbene–Gold(I) Complexes. *Chem. Mater.* **2021**, *33* (24), 9588–9600.
- 5- Cui, L.; Du, M.; Guo, S. Preparation, Characterization and Stability Studies of Gold Nanoparticles Capped by 1,2,3-Triazole-Based Mesoionic Carbenes. *ChemistrySelect* **2022**, *7* (34). e202201999



**Thematic Session :** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords :** metal-support interactions, methanol synthesis, CO<sub>2</sub> valorization

**Disciplinary fields involved :** Chemistry, Materials science, Heterogeneous Catalysis

**Sustainable Development Goals\* eventually involved in your research:** Climate action (Goal 13) (CO<sub>2</sub> valorization)

## Understanding the interactions in CuO-ZnO-ZrO<sub>2</sub> catalyst

Diego Jose Rua Gonzalez<sup>1</sup>, Ksenia Parkhomenko<sup>1</sup>, Valentin L'hospital<sup>2</sup>, Anne-Cécile Roger<sup>1</sup>

1. UMR 7515 CNRS, Energy and Fuels for a Sustainable Environment Group, The Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France
2. UMR 5256 CNRS, Catalyst and Process Engineering Group, The Research Institute on Catalysis and Environment of Lyon (IRCELYON), 2 Avenue Albert Einstein, 69626 Villeurbanne, France

The objective of this work is in deep study of the methanol synthesis catalyst CuO-ZnO-ZrO<sub>2</sub> and understanding of the interactions between the components on the nano-level. Two different methods of catalytic materials synthesis were used: a batch way and using a microfluidic system. Firstly, all the single, binary and ternary precursors before calcination were prepared. In the second step the precursors were calcined. All the materials before and after calcination were fully characterized and the catalytic tests of methanol synthesis via hydrogenation of CO<sub>2</sub> were performed.

It was discovered that the synthesis in a microfluidic system greatly improves the affinity between the components during the preparation of binary and ternary precursors. It was possible to obtain much more homogeneous materials than using the batch synthesis. Intimate and strong interactions between copper, zinc and zirconium as well as the unique flower-like morphology with high specific surface area and high copper metallic surface area were achieved. Thus the catalyst prepared in a microfluidic system presented a good CO<sub>2</sub> conversion of 21.4 % along with a methanol selectivity of 33 %, leading to a record never published before methanol productivity of 1135 g<sub>MeOH</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 280 °C, 50 bar and a GHSV of 25,000 h<sup>-1</sup> (STP).<sup>1</sup> The study on the nano-scale of the metal-support interactions over methanol synthesis catalysts prepared in a microfluidic system will be presented for the first time.

### References:

<sup>1</sup> V. L'hospital *et al*, Fuel 319 2022 123689, <https://doi.org/10.1016/j.fuel.2022.123689>

### Acknowledgment:

The authors acknowledge the ANR (project DIGAS N°ANR-14-CE05-0012) and The Government of Colombia (stipend call 860 from 2019 attributed to Diego Jose Rua Gonzalez) for the financial support.

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** Silicon particles, in-situ electron microscopy, hydrogen silsesquioxane, dewetting process

**Disciplinary fields involved:** Chemistry, Physics

## Understanding the mechanisms involved in the formation of silicon particles from the thermal decomposition of hydrogen silsesquioxane: an in situ study by TEM

Cynthia Cibaka-Ndaya<sup>1</sup>, Kevin O'Connor<sup>2</sup>, Emmanuel Opeyemi Idowu<sup>1</sup>, Jonathan G.-C. Veinot<sup>2</sup>, Lucian Roiban<sup>3</sup>, Glenna L. Drisko<sup>1</sup>

1. ICMCB, UMR 5026, CNRS, Univ. Bordeaux, Bordeaux INP, Pessac F-33600, France
2. Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada
3. MATEIS, UMR 5510, Univ Lyon, INSA Lyon, Université Claude Bernard Lyon 1, CNRS, 69621 Villeurbanne, France

Hydrogen silsesquioxane (HSQ) compounds, often applied as a resist in lithography processes, were previously demonstrated to be efficient precursors for the preparation of silicon particles. (1–3) In this approach, spherical silicon particles result from the thermal decomposition of HSQ at high temperatures ( $> 1000^{\circ}\text{C}$ ), which leads to its disproportionation into crystalline Si particles embedded in a matrix of silica. The particles are then collected after etching the silica matrix with HF. The thermal processing temperature can be adjusted in order to tailor the size of the resulting silicon particles from  $\approx 3$  to  $\approx 200$  nm. (2,3) In a previous study, the formation of Si nanostructures through this route has been investigated using spectroscopic and diffraction techniques, which supported the growth and increased crystallinity of the silicon nanodomains above  $900^{\circ}\text{C}$ . (4)

The purpose of the present study is to deepen the understanding of the mechanisms involved in silicon particle formation and growth. To achieve this, in situ observations of HSQ decomposition at high temperatures were performed by environmental transmission electron microscopy. While the nucleation of Si nanodomains was observed from  $1000^{\circ}\text{C}$ , confirming the conclusions of the work in ref (4), particle growth mechanisms were also identified. The coalescence of small particles into larger ones was observed. In addition, above the melting point of silicon, silicon particles evolved in a liquid phase, growing while moving inside the matrix towards the surface. These real time observations were complemented with SEM analysis of the treated HSQ and in situ XRD measurements up to  $1200^{\circ}\text{C}$ .

### References:

1. Hessel CM et al. Chem Mater. 1 déc 2006;18(26):6139- 46.
2. Clark RJ et al. Chem Mater. 10 janv 2017;29(1):80- 9.
3. Milliken S et al. Nanoscale. 14 oct 2021;13(39):16379- 404.
4. Hessel CM et al. J Phys Chem C. 1 mai 2007;111(19):6956- 61.

### Acknowledgments:

This project is supported by funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (*Scatter*, Grant agreement No. 948319). The authors acknowledge the French national project METSA for providing them with access to the microscope platform of CLYM in Lyon. David Montero performed FEG-SEM observations at the Institut des Matériaux de Paris Centre (IMPC FR2482), which was co-funded by Sorbonne Université, CNRS and by the C'Nano projects of the Région Ile-de-France.

**Thematic Session:** Nanochemistry, Nanoparticles, Nanocatalysis

**Keywords:** organometallic approach, molybdenum, oxide, sulfide, nanoparticles

**Disciplinary field involved:** Chemistry

**Sustainable Development Goals\* eventually involved in your research:** Industry, Innovation, and Infrastructure (Goal 9)

## Using Mo(0) complex as highly reactive platform for the synthesis of molybdenum oxide nanoparticles under mild conditions

**Martin Jakoobi<sup>1\*</sup>, Guillaume Carnide<sup>1</sup>, Laure Vendier<sup>1</sup>, Christian Bijani<sup>1</sup>, Anne-Françoise Mingotaud<sup>2</sup>, Richard Clergereaux,<sup>3</sup> Myrtil L. Kahn<sup>1\*</sup>**

1. LCC-CNRS, Université de Toulouse, INPT, UPS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France
2. Laboratoire des IMRCP, Université de Toulouse, CNRS UMR 5623, Université Paul Sabatier, 118, route de Narbonne, F-31062 Toulouse, Cedex 09, France
3. LAPLACE, CNRS UMR5213, Université de Toulouse, 118 route de Narbonne, 31062, Toulouse, France

Since the establishment of nanoparticle (NP) synthesis using organometallic approach by B. Chaudret and J. S. Bradley, this methodology has become the go-to tool for many research groups, ours included, to synthesize these nanoscale objects under mild conditions, while selectively controlling their size and shape. To this day, this methodology has been mainly applied on the synthesis of late transition metal and metal oxide NPs (group 8-12) from precious (Ru, Rh, Pd, Pt, Ag, Au) and first-row (Fe, Co, Ni, Cu, Zn) metal complexes.<sup>1,2</sup> At the same time, the development of suitable early transition metal complexes (group 3-7) for the preparation of corresponding oxide, sulfide, etc. NPs has attracted only sporadic attention. Here we would like to report our findings on the use of highly reactive Mo(0) complex for the synthesis of <10 nm molybdenum oxide (MoO<sub>x</sub>) NPs at room temperature. These results illustrate how the choice of solvent, the ligand backbone length and concentration affect the colloidal stability of these MoO<sub>x</sub> NPs. Additionally, we will further demonstrate the reactivity of our Mo(0) system towards other heavier chalcogenes, and other non-transition metal elements and reagents.<sup>3</sup>

### References:

1. Amiens, C.; Chaudret, B.; Ciuculescu-Pradines, D. ; Colliere, V. ; Fajerweg, K. ; Fau. P. ; Kahn. M. ; Maisonnat. A. ; Soulantica. K. ; Philippot. K. *New J. Chem.* **2013**, 37, 3374.
2. Cerezo-Navarrete, C.; Lara, P.; Martínez-Prieto, L.M. *Catalysts* **2020**, 10, 1144.
3. Jakoobi, M.; Carnide, C.; Vendier, L.; Bijani C.; Mingotaud, A.-F.; Clergereaux, R. ; Kahn, M. L. *manuscript in preparation*

### Acknowledgment:

This work was carried out in the framework of the RIF project funded by BPI France.

**Thematic Session:** Nanomaterials for Energy

**Keywords:** 4H-SiC, WBG, CTLM, ion implantation

**Disciplinary field involved:** semiconductors

**Sustainable Development Goals\* eventually involved in your research:** Industry, Innovation & Infrastructure (Goal 9) & Responsible Consumption and Production (Goal 12)

## Improving electrical contact of highly *n*-type doped 4H-SiC by Circular Transfer Length Method

**E. USUREAU<sup>1</sup>, E. FRAU<sup>2</sup>, M. MARTEAU<sup>3</sup>, J.F. BARBOT<sup>3</sup>, M. LAZAR<sup>1</sup>, C. BRYLINSKI<sup>2</sup>**

1. *Laboratory Light, nanomaterials & nanotechnologies (L2n), CNRS EMR 7004, University of Technology of Troyes, 12 rue Marie Curie, 10004 Troyes, France*
2. *Laboratoire des Multimatériaux et Interfaces (LMI), Université Claude Bernard LYON 1, UMR CNRS 5615, 43, bd du 11 Novembre 1918, 69622 Villeurbanne, France*
3. *Institut Pprime UPR 3346, 11 Bd Marie et Pierre Curie- TSA 41123, 86073 Poitiers cedex 9*

Silicon Carbide (SiC) is a wide bandgap (WBG) semiconductor commonly used in power electronics and more and more studied today for its application in optoelectronics and nanophotonics. However, despite its technological maturity, electrical contacts on 4H-SiC need to be improved, on the both Si and C faces. Therefore, we developed a new method to evaluate ohmic contacts based on the circular transfer length method (CTLM) [1], which we applied on *n*-type highly doped 4H-SiC semi-insulating wafers.

On both Si and C faces, box nitrogen profiles were created by multi-energy (30-160 keV) ion implantations in order to obtain a plateau concentration of  $5 \times 10^{19} \text{ cm}^{-3}$  on  $0.3 \mu\text{m}$  from the surface. An activation annealing was performed at  $1700^\circ\text{C}/30\text{min}$  in a dedicated RTP furnace using a pyrolysed C-cap.

Test-structures are created to estimate the specific contact and sheet resistances via proportional equations. The conductive layer for ohmic contact was obtained by a first nickel-based metallization through an RTA annealing at  $900^\circ\text{C}$  during 90s. An over-metallization (Ti/Ni/Au) was added to enhance the potential repartition. By photolithographic process SiC highly N-doped uncovered rings of different lengths (*d*) are therefore obtained. Current-voltage (I-V) measurements are performed with a two-point probe-station. A conductive behavior is obtained showing that electrical contact has been optimized (cf. Fig. 1).

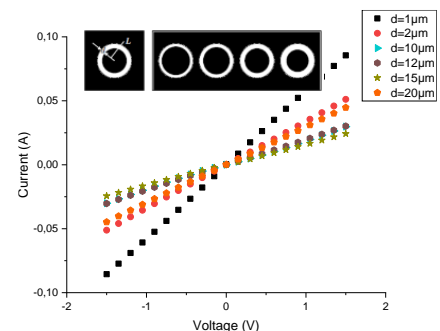


Fig. 1 I-V measurements on N-doped 4H-SiC



# C'Nano

THE NANOSCIENCE MEETING

# Positiers

March, 15, 16 and 17

# 2023



**References:**

[1] Dieter K. Schroder, Semiconductor Material and Device Characterization, 3rd Edition, pp. 840. ISBN 0-471-73906-5. Wiley-VCH, December 2005.

**Acknowledgment:**

This work was financially supported by the Grand-Est region from France and the SATT SAYENS (Maison Régionale de l'Innovation, 64 A rue Sully 21000 Dijon [www.sayens.fr](http://www.sayens.fr)). The experiments were carried out within the Nanomat platform ([www.nanomat.eu](http://www.nanomat.eu)).



**Thematic Session:** Nanotechnology for cleaning environment

**Keywords:** NO reduction, hydrogen, SCR

**Disciplinary field involved:** Chemistry

## Catalytic NO<sub>x</sub> treatment from hydrogen internal combustion engine.

**A. Ben Attia<sup>1</sup>, J.B. Petit<sup>1</sup>, F. Can<sup>1</sup>, X. Courtois<sup>1</sup>**

1. *Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), University of Poitiers, CNRS UMR 7285, TSA51106 – F86073 Poitiers Cedex 9, France*

The implementation of batteries or a fuel cell as a decarbonised propulsion mode for heavy trucks remains an issue. One alternative solution lies in the development of green hydrogen internal combustion engines. Nevertheless, traces of NO<sub>x</sub> may persist during lean-burn combustion. Traditional three way catalysts (TWC) are not adapted for lean mixture treatment and the current Diesel deNO<sub>x</sub> treatment using urea (NH<sub>3</sub>-SCR) is constraining and leads to some CO<sub>2</sub> emission. The most attractive approach for H<sub>2</sub>-ICEs remains the NO<sub>x</sub> selective catalytic reduction by H<sub>2</sub> (H<sub>2</sub>-SCR), but NO<sub>x</sub> elimination over a large temperature range (150°C-500°C) is challenging. This study, based on very low platinum loading (0,1<sub>wt</sub>%) catalysts supported on silica-alumina, aims to investigate the influence of (i) iron addition with the aim to promote the NO<sub>x</sub> hydrogenation and (ii) basic oxide addition (Ba, Ca, K) to favour the adsorption of N oxidised species (NO<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>). The maximum NO<sub>x</sub> conversion is observed at 150°C on Pt/Si-Al. It is shifted to 200°C with iron and barium addition and the catalyst is significantly deactivated by potassium addition. Interestingly, calcium addition mainly leads to a decrease in the N<sub>2</sub>O selectivity, while the basic behaviour of the catalysts (evaluated by NO<sub>2</sub> TPD) appears similar whatever basic oxide addition.

### Acknowledgment:

The authors acknowledge financial support from the French National Research Agency (H to Clean project, ANR-21-CE05-0012), the European Union (ERDF) and Région Nouvelle Aquitaine

**Thematic Session:** Nanobiosciences

**Keywords:** Gold nanoparticles, Magnetic beads, Immunosensor, Microfluidic chip

**Disciplinary fields involved:** Chemistry, Physics, Biology

**Sustainable Development Goals\* eventually involved in your research:** Good Health and Well-Being (Goal 3)

## Magneto-plasmonic biosensing: from benchtop spectrometer readout to 3D-printed microfluidic devices

**Mona Soroush<sup>1,2</sup>, Walid Ait Mammam<sup>1</sup>, Axel Wilson<sup>1</sup>, Hedayatollah Ghourchian<sup>2</sup>, Michèle Salmain<sup>3</sup>, Souhir Boujday<sup>1</sup>**

1. *Laboratoire de Réactivité de Surface, Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique : UMR7197, Paris, France*
2. *Laboratory of Bioanalysis, Institute of Biochemistry & Biophysics, University of Tehran, P.O. Box 13145-1365, Tehran 1417614335, Iran*
3. *Institut Parisien de Chimie Moléculaire – Chimie Moléculaire de Paris Centre, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique : UMR8232, Sorbonne Université – France*

Monitoring biomarkers in clinical samples allows to predict the onset, development, and severity of diseases. Biosensors are among the most promising devices for detection of diseases-related biomarkers thanks to their capability to realize rapid, sensitive, label-free, cost-effective, and real time detection [1]. The high surface to volume ratio of the microfluidic device can enhance mass transport, resulting in shorter assay time and increased detection sensitivity.

In this project we have developed a magneto-plasmonic biosensor for the immunodetection of antigens in minute sample volume. Both spherical gold nanoparticles (AuNP) and magnetic beads (MB) were conjugated to goat anti-IgG antibody (Ab) capable of recognizing a model target, rabbit IgG (rIgG) (Fig.1 (a)). The AuNP bioconjugate was used as optical detection probe while the MB one was used as capture probe. Addition of target analyte followed by detection probe resulted in the formation of a sandwich immunocomplex (Fig.1 (b)) which was separated from the unbound AuNP-Ab conjugate by application of an external magnetic field. The readout was done either in direct or in indirect way by measuring the UV-Visible spectrum of each fraction in a specially designed microcell (Fig.1 (a)). Dose-response curves were established from the optical signal of the immunocomplex and unbound AuNP-Ab conjugate fractions (Fig.1 (c)).

To go further towards the development of a stand-alone device, we designed a microfluidic cell that integrates the magnetic separation and readout steps in a single device (Fig.1 (a)). Transposing the assay to a microfluidic chip enabled a dramatic decrease in the assay sensitivity with a LoD in the ng/mL range (Fig.1 (d)) [2]. In the future this immunosensor could be readily translated to more biological meaningful biomarkers related to health and/or food security.

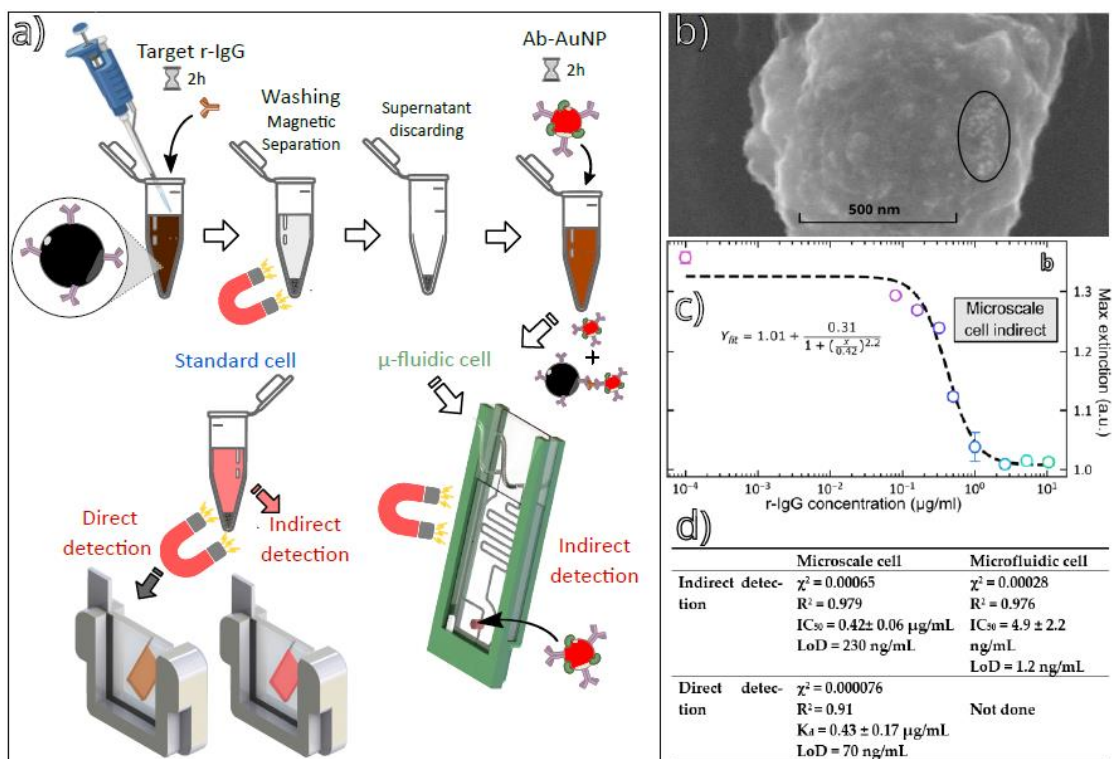


Figure 1 a) Schematic presentation of the general principle of magneto-plasmonic immunoassay, b) SEM image (15 kV, 10.3 mm, 80000 $\times$ ) of the magneto-plasmonic immunocomplex in the presence of 1  $\mu$ g/mL of r-IgG and a black circle showing the presence of AuNPs, c) dose-response curve plotted from the maximum extinction at 530 nm vs. rabbit IgG concentration, d) Fitting parameters and analytical performances of the magneto-plasmonic immunosensor in the direct and indirect formats.

## Références:

- 1- Wang, Yijia, et al. "Investigation of phase SPR biosensor for efficient targeted drug screening with high sensitivity and stability." *Sensors and Actuators B: Chemical* 209 (2015): 313-322.
- 2- Soroush, M., Ait Mammour, W., et al. "Design and Optimization of A Magneto-Plasmonic Sandwich Biosensor for Integration within Microfluidic Devices." *Biosensors* 12.10 (2022): 799.

## Acknowledgments:

All my acknowledgments to my co-authors including my supervisors and all people contributed in any way to this work.

**Thematic Session:** Nanobiosciences

**Keywords:** Energy Transfer, Biodetection, Whispering Gallery Modes, Quantum dots

**Disciplinary fields involved:** Chemistry, Physics

**Sustainable Development Goals\* eventually involved in your research:** Good Health and Well-Being (Goal 3)

## DNA biodetection assay based on Whispering Gallery Mode Energy Transfer

Nour Alkastntini,<sup>1</sup> Subha Jana,<sup>1</sup> Xiangzhen Xu,<sup>1</sup> Nina Melnychuk,<sup>2</sup> Elisabete Cruz Da-Silva,<sup>2</sup> Andreas Reisch,<sup>2</sup> Andrey Klymchenko,<sup>2</sup> Thomas Pons<sup>1</sup>

1. *Laboratoire Physique et Etude des Matériaux, ESPCI Paris, PSL Research University ; Sorbonne Université ; CNRS UMR8213, Paris, France*
2. *Laboratoire de Bioimagerie et Pathologies, Université de Strasbourg ; CNRS UM7021, Strasbourg, France*

Fluorescence-based biosensors have emerged in a response to demand for specific and simple detection in biomedical diagnostics. Förster resonance energy transfer (FRET) based assays present multiple advantages such as rapid, easy to use and highly specific analysis. However, this technique has a strong dependence on the donor-acceptor distance ( $\sim 10$  nm) and has a limit of detection usually lying in the nM range. To overcome this limitation, we introduce Whispering Gallery Mode Energy Transfer, a highly sensitive biosensing platform based on energy transfer between polymeric microcavities loaded with semiconductor quantum dots as energy donors and dye-loaded polymeric nanoparticles as energy acceptors. The quantum dot emission couples efficiently to Whispering Gallery Modes (WGMs) within the microcavities. This generates an evanescent field at the surface of the microcavities, which spread up to a few tens to hundreds of nm above the cavity surface, enabling a wide range of distance for energy transfer. In addition, the high-quality factor of the WGMs and their large surface allows the detection of analytes with small concentration. Moreover, the high absorption cross-section and brightness of the dye-loaded nanoparticles as energy acceptors ensures optimal energy transfer efficiency and sensitivity. Here, we present the surface functionalization of microcavities and the development of a specific DNA biosensing assay based on this novel biodetection strategy, for the detection of survivin, a cancer biomarker, as an example.



## Thematic Session: Nanobiosciences

**Keywords:** Biosensor, SPR, micro-RNAs, Surface Chemistry, nanostructuring

**Disciplinary fields involved:** Physics, Chemistry, Biology

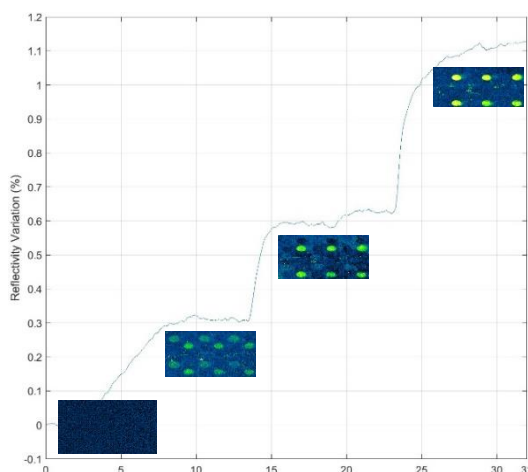
### SPR Biosensor for the detection of micro-RNAs

Coline BELTRAMI<sup>1,2,3</sup>, Laurence CONVERT<sup>1,2</sup>, Julien MOREAU<sup>3</sup>, Jean-François BRYCHE<sup>1,2</sup>, Paul CHARETTE<sup>1,2</sup>, Michael CANVA<sup>1,2</sup>

1. Laboratoire Nanotechnologies Nanosystèmes (LN2) ; CNRS IRL-3463, Université de Sherbrooke ; 3IT, Canada.
2. Institut Interdisciplinaire d'Innovations Technologiques (3IT), Université de Sherbrooke, Canada.
3. Laboratoire Charles Fabry (LCF) ; CNRS UMR-8501, Institut d'Optique Graduate School (IOGS), Université Paris-Saclay, France.

In a situation of organ donation from a brain deceased donor, the brain death seriously compromises the number and quality of organs for transplantation because of an intense systemic inflammatory response happening throughout the donor body: the cytokine storm<sup>1</sup>. The lack of evidence and contradictory results of the current therapeutics (steroids, broad spectrum antibiotics...) support the need for a more personalized immunosuppressive treatment to better preserve the organs<sup>2</sup>. The purpose of my work is to use Surface Plasmon Resonance Imaging (SPRI) combined with surface functionalization and structuration of the biochip to detect the inflammatory biomarkers (micro-RNAs) correlated with the appearance and evolution of the cytokine storm<sup>3</sup>. This biosensor will need to be able to reach a detection limit in the range of the femtomolar for DNA then RNA as small as

only 20 pairs of bases. Organ donation from a brain deceased donor being a timely sensitive medical process, the sensor needs to give a result in a real-time fashion (under an hour) and to analyze complex medium (human plasma). In order to achieve those previously stated objectives, we need to use an antifouling surface chemistry to work in complex medium and combine several amplification methods to achieve the detection limit. To that end, chemical amplification by big proteins attachment and nanostructured bi-material (Au-SiO<sub>2</sub>)<sup>4</sup> SPR substrates are the first technics of interest to be tested.



### References:

1. Watts, R. P., Thom, O. & Fraser, J. F. Inflammatory Signalling Associated with Brain Dead Organ Donation: From Brain Injury to Brain Stem Death and Posttransplant Ischaemia Reperfusion Injury. *J Transplant* 2013, 521369 (2013).
2. Ball, I. M. et al. Management of the neurologically deceased organ donor: A Canadian clinical practice guideline. *CMAJ* 192, E361–E369 (2020).
3. Clément, A.-A. et al. Time-course full profiling of circulating miRNAs in neurologically deceased organ donors: a proof of concept study to understand the onset of the cytokine storm. *Epigenetics* 1–16 (2022) doi:10.1080/15592294.2022.2076048.
4. Palazon, F. et al. Orthogonal chemical functionalization of patterned gold on silica surfaces. *Beilstein J. Nanotechnol.* 6, 2272–2277 (2015).

**Thematic Session:** Nanobiosciences

**Keywords:** Theranostics, SPIO, Macrophages, MRI, Cancer

**Disciplinary fields involved:** Chemistry, Physics, Biology

## Development and *in vitro* analysis of SPIO for theranostic purposes in cancer

Alan Courteau<sup>1,2</sup>, Méline Roche<sup>1</sup>, Camille Petitot<sup>1</sup>, Alexandra Oudot<sup>1</sup>, Chloé Gervasoni<sup>3</sup>, Pierre-Simon Bellaye<sup>1</sup>, Richard Decréau<sup>4</sup>, Jérémy Paris<sup>3</sup>, Bertrand Collin<sup>1,4</sup>, Alexandre M. M. Dias<sup>1</sup>

1. Plateforme d'Imagerie et de Radiothérapie Précliniques, Service de Médecine Nucléaire, Centre Georges-François Leclerc, 1 rue du Professeur Marion, 21079 Dijon, France
2. ImViA Laboratory, EA 7535, University of Burgundy, 21000 Dijon, France
3. SONSAS, 21000 Dijon, France ([www.sonsas.com](http://www.sonsas.com))
4. Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS/uB 6302, 21079 Dijon, France

Over the last 20 years, superparamagnetic iron oxide nanoparticles (SPIO) have been widely explored for a variety of biomedical applications. Notably, thanks to their compliance with magnetic resonance imaging (MRI) combined with their capacity to target the immune system through macrophage polarization, SPIO are promising theranostic probes that could be used as a therapeutic lead in solid malignancies treatment, in which macrophages play an important role. The objective of our study was to evaluate biophysical characteristics and *in vitro* macrophages polarization induction capabilities of three types of SPIONs in colloidal suspensions. Three magnetite-based core nanoparticle solutions were prepared (SONSAS, Dijon, France): without coating (SPIO), with an amine coating (SPIO-NH<sub>2</sub>) and with a carboxylic coating (SPIO-COOH). The contrast enhancement capability of SPIO was determined by a relaxivity assay based on multiple spin echo acquisitions performed on the 7 T magnet of a preclinical simultaneous PET/MR system (MR Solutions, Guildford, UK). Moreover, an *in vitro* murine macrophage polarization model (J774A.1 cells) was set up to assess the effect induced by SPIO on macrophage polarization. Our study demonstrates that SPIO-NH<sub>2</sub> displayed an acceptable compromise between relaxivity and linear working range of the relaxation rate plotted against concentration. In addition, we found that SPIO-NH<sub>2</sub> favored macrophage polarization towards a pro-inflammatory M1-like phenotype known for its anti-tumoral properties. Therefore, SPIO-NH<sub>2</sub> might offer both physical and biological promising properties for *in vivo* applications in oncology. SPIO-NH<sub>2</sub> design modifications are currently performed to improve its macrophage targeting efficiency.

### Acknowledgment:

This research was funded by a French Government grant managed by the French National Research Agency under the program "Investissements d'Avenir" with reference ANR-10-EQPX-05-01/IMAPPI Equipex. It was also supported by the Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB UMR CNRS 6302) and by the Centre Georges-François Leclerc (Preclinical imaging and radiotherapy platform, nuclear medicine department). This work was performed within Pharm'Image, a regional center of excellence in pharmaco-imaging.



