



Wednesday, November 24th

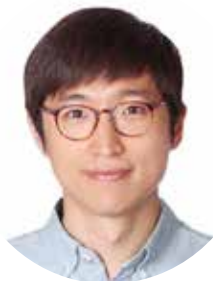
Session Nanochemistry & Nanoparticles

10:50 – 11:20 Keynote

Jong-Wook KIM, Ecole Polytechnique – LPMC,
France

Abstracts

Keynote Speakers



Jongwook KIM

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Biography

J. Kim did his undergraduate study at KAIST (2006), master study at Ecole Central Paris (2009), and PhD at Ecole Polytechnique (2013) on the topic of 'Colloidal dynamics of luminescent anisotropic nanocrystals'. Then he did a post-doctoral research at Lawrence Berkeley National Laboratory (LBNL) (2014~2015) and Univ. of Texas at Austin (2015) on the topic of 'Plasmonic semiconductor nanocrystals and their application to electrochromic smart windows'. Since 2016, he has been continuing his professional career at the condensed matter physics lab (LPMC) at Ecole Polytechnique. He is developing both the chemical synthesis of various types of nanocrystals and their in-situ micro-spectroscopy in biomedical environments and for applications to sustainable energy.

TAILORING ANISOTROPIES IN NANOCRYSTALS

Recent nanocrystal research has discovered the new material properties emerging from size, shape, surface, and interface, which provided a variety of novel functionalities in high-tech devices. Contrarily, the principal impacts of the intrinsic structure of materials, especially the anisotropic physico-chemical properties, are more and more underestimated. Many of the profound earlier studies on bulk materials are overlooked while investigating the same compositions in nanoscale. Such a tendency limits rational understanding of the nanomaterials and their benefits.

In this presentation, it will be discussed the strategies to redesign anisotropic nanomaterials for their nano-properties and intrinsic properties to synergistically collaborate in order to achieve unprecedented functionalities. As a first example, plasmonic semiconductor nanocrystals are presented. The localized surface plasmon resonance (LSPR), commonly investigated with metal nanoparticles, has been controlled with the particle size and shape. Instead of metal, we use semiconductor that allows to synthetically tune the doping level and the structure of matrix. By deliberately controlling the crystal phase and morphology of the semiconductor nanocrystals, we achieve a wide spectral range (from VIS to IR) and post-synthetic modulation of LSPR [1,2]. The second example is the anisotropic rare-earth phosphor nanocrystals. Rare-earths are extensively used for energy sustainability (e.g. windmills, electric cars, batteries, catalysts, and lightings). Their unique properties originate from the protected f-orbital electrons so that the bulk properties are unchanged even in nanoscale. We combine such a stability of the polarized rare-earth luminescence with the dynamic behavior of anisotropically shaped nanocrystals. As-designed rare-earth nanocrystal phosphors can be used to monitor complex motions of micro-biosystems and also for microfluidic analysis essential for health care [3,4].

References

[1] Nano Lett. 15, 5574-5579 (2015)

[2] Nano Lett. 16, 3879-3884 (2016)

[3] Nature Nanotechnology. 12, 914-919 (2017)

[4] JACS. 140, 9512-9517 (2018)

Keywords: synthesis; tungsten oxide; plasmon; lanthanide; phosphor; polarization.

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The Nanoscience Meeting

TOULOUSE

Centre des congrès Pierre Baudis

December, 8, 9 and 10



Thematic Session: Nanochimie et nanomaterials

Keywords: iron stearates, decomposition mechanisms, composition and size mastering, growth and oxidation kinetics

Impact of precursor, solvent and ligand on the size and composition of iron oxide nanoparticles

Geoffrey Cotin, Francis Perton, Céline Kiefer, Barbara Freis, Damien Mertz, Benoit Pichon, Sylvie Begin

Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, F-67034 Strasbourg

Iron oxide nanoparticles (IONPs) display broad range of applications and in particular, are commercialized as MRI contrast agents and when their size is ~ 20 nm, they may provide also promising therapy by magnetic hyperthermia. The synthesis of IONPs with size and composition suitable for magnetic hyperthermia is currently a challenge as synthesis conditions necessary to reach such high sizes often lead either to core-shell composition or to a spinel composition but with the presence of defects. Both the core-shell composition and the presence of defect affect the magnetic hyperthermia performance of these NPs. The control of the IONPs size and composition is crucial to ensure adapted magnetic properties and so high heating power by magnetic hyperthermia.

To face these challenges, we synthesized ironII and ironIII stearates determined their structure and investigated their thermal decomposition mechanisms by IR and Mössbauer spectroscopies in temperature, MALDI-TOF, cryoTEM, liquid AFM and SAXS and by following the germination and growth steps by in-situ TEM in temperature. We demonstrated that the nuclei composition is wüstite and described the reduction mechanisms. Then, the composition of NPs with mean size around 20 nm was shown to depend on the size of $Fe_{1-x}O$ nuclei and on synthesis parameters such as the ligands and nature of solvents which will impact the oxidation and growth kinetics of the nuclei. In addition, the temperature synthesis affects the IONPs surface properties affecting the functionalisation step. Such studies have allowed to establish synthesis conditions leading to 20 nm IONPs with homogeneous spinel composition.

W. Baaziz, B.P. Pichon, S. Fleutot, Y. Liu, C. Lefevre, J.-M. Greneche, M. Toumi, T. Mhiri, S. Begin-Colin, Magnetic Iron Oxide Nanoparticles: *J. Phys. Chem. C*. 118 (2014) 3795

A. Walter, C. Billotey, A. Garofalo, C. Ulhaq-Bouillet, C. Lefèvre, J. Taleb, S. Laurent, L. Vander Elst, R.N. Muller, L. Lartigue, F. Gazeau, D. Felder-Flesch, S. Begin-Colin, *Chem. Mater.* 26 (2014) 525

G. Cotin, C. Kiefer, F. Perton, D. Ihiwakrim, C. Blanco-Andujar, S. Moldovan, C. Lefevre, O. Ersen, B. Pichon, D. Mertz, S. Bégin-Colin, *Nanomaterials*. 8 (2018) 881.

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G. Cotin, C. Kiefer, F. Perton, M. Boero, B. Özdamar, A. Bouzid, G. Ori, C. Massobrio, D. Begin, B. Pichon,
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Thematic Session: Nanochemistry & Nanoparticles

Keywords: magnetite nanoparticles; nucleation mechanisms; in-situ SAXS; nucleation theory

"Non-classical" nucleation of oxide nanoparticles in solution: implications on structure control

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Crystallization from solution is commonly described by classical nucleation theory [1], although this ignores that crystals often form via disordered nanostructures [2]. As an alternative, the classical theory remains widely used in a "multi-step" variant, where the intermediate nanostructures merely introduce additional thermodynamic parameters [3]. But this variant still requires validation by experiments addressing indeed proper time and spatial scales (ms, nm). We used in situ X-ray scattering to determine the mechanism of magnetite crystallization and in particular how nucleation propagates at the nanometer scale within amorphous precursors [4]. We find that the self-confinement by an amorphous precursor slows down crystal growth by two orders of magnitude once the crystal size reaches the amorphous particle size (c.a. 3 nm). Thus, not only the thermodynamic properties of transient amorphous nanostructures, but also their spatial distribution determine crystal nucleation.

References:

- [1] Kelton, K.; Greer, A. L. *Nucleation in Condensed Matter: Applications in Materials and Biology*; Pergamon materials series; Elsevier: Amsterdam, 2010.
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Acknowledgment:

SOLEIL synchrotron for beamtime, The French National Research Agency (ANR-14-CE08-0003, ANR-10-LABX-0035), the Max Planck Society, the DFG (DFG-ANR Project FA 835/10-1), and the European Research Council (256915-MB2).



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Thematic Session: Nanochemistry & Nanoparticles

Keywords: upconversion nanoparticles, $\text{RE}_2\text{O}_2\text{S}$, $\text{RE}_2\text{O}_2\text{S}@Na\text{REF}_4$.

Controllable synthesis of ultra-small $\text{RE}_2\text{O}_2\text{S}$ and $\text{RE}_2\text{O}_2\text{S}@Na\text{REF}_4$ heterogeneous core-shell nanoparticles

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2. IMRCP, Université de Toulouse, UPS, CNRS, Toulouse, France

Lanthanide-doped upconversion nanoparticles have been studied for more than two decades due to their unique optical properties and electronic structures.^[1] Although a few reports have described the synthesis of rare earth oxysulfide ($\text{RE}_2\text{O}_2\text{S}$) nanoparticles (which are good host candidates thanks to their low phonon energy)^[2,3], there is still a need to develop a more general approach to prepare $\text{RE}_2\text{O}_2\text{S}$ nanoparticles. Here we provide an improved high-temperature decomposition method to synthesize 15 kinds of ultra-small $\text{RE}_2\text{O}_2\text{S}$ (RE=Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) nanoparticles with a mean size varying from 3 to 11 nm. This strategy was optimized through a variety of impact factors, such as solvents ratio, influence of the amount of sulfur source and LiOH, reaction temperature and time. When doped with adequate sensitizing and activating ions, these lanthanide-doped $\text{RE}_2\text{O}_2\text{S}$ nanoparticles show measurable but poor upconversion luminescence efficiency, which is consistent with surface-based quenching typical of ultra-small particles. To solve this issue, a novel core-shell architecture engineering strategy was proposed, in which 4 nm thickness of NaYF_4 shell first successfully coated on the surface of the ~6 nm $\text{Gd}_2\text{O}_2\text{S}:20\%\text{Yb},1\%\text{Tm}$ nanoparticles. Then we recorded 836 times enhancement of upconversion luminescence intensity of $\text{Gd}_2\text{O}_2\text{S}:20\%\text{Yb},1\%\text{Tm}@Na\text{YF}_4$ nanoparticles compared with that of the core nanoparticles. Unexpectedly, this strategy can be expanded to synthesize other 14 kinds of $\text{Gd}_2\text{O}_2\text{S}:20\%\text{Yb},1\%\text{Tm}@Na\text{REF}_4$ (RE=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) nanoparticles. The epitaxial growth mechanism was systematically investigated. In a summary, we demonstrate a versatile approach for synthesis of ultra-small $\text{RE}_2\text{O}_2\text{S}$ nanoparticles and $\text{RE}_2\text{O}_2\text{S}@Na\text{REF}_4$ heterogeneous core-shell nanoparticles, respectively. More importantly, these findings open up a new avenue for potential application of lanthanide-doped $\text{RE}_2\text{O}_2\text{S}@Na\text{REF}_4$ heterogeneous core-shell upconversion nanoparticles.

References:

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[2] Fei Zhao, Mei Yuan, Wen Zhang and Song Gao, *J. Am. Chem. Soc.* 2006, 128, 11758-11759.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: metal oxide nanoparticles, electrosynthesis, *in situ* characterization, single entity electrochemistry

Ag₂O nanoparticles electrosynthesis and characterization at the individual scale

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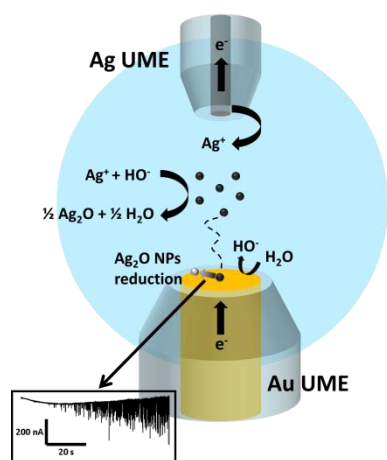


Figure 1 – Principle for the simultaneous generation/collection of Ag₂O NPs.

Metal oxide nanoparticles are of major importance in many fields of nanotechnology because of their remarkable physicochemical properties. To establish more precisely the structure-reactivity relationship of the NPs, strategies allowing to produce a diversity of such NPs and to characterize their physicochemical properties simultaneously must be developed. Inspired from previous work¹, we propose to synthesize electrochemically silver oxide NPs using a silver sacrificial ultramicroelectrode as a source of silver ions facing a second electrode used to increase locally the pH of the solution. It leads to the precipitation of silver oxide nanoparticles in the confined space in between both electrodes. The condition of formation and their characterization have been extensively studied *in situ* by dark field microscopy and electrochemically in a generation/collection mode through the reductive nanoimpact strategy² (Figure 1). This original approach is used to decipher the NPs nucleation and growth mechanism. This novel approach could be later applied to more complex systems involving other transition metals and constitutes a versatile method for the generation and simultaneous characterization of diverse nano-objects.

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- 1 J.-M. Noël, M. Miranda Vieira, V. Brasiliense, J.-F. Lemineur, C. Combellas and F. Kanoufi, *Nanoscale*, 2020, 3227–3235.
- 2 Y.-G. Zhou, N. V. Rees and R. G. Compton, *Angew. Chemie Int. Ed.*, 2011, **50**, 4219–4221.

Thematic Session: Nanomaterials

Keywords: indium sulfide ultra-thin nanoribbons, hexagonal indium sulfide nanoplates, shape-controlled synthesis, TEM, SAXS

Shape-controlled synthesis of ultra-thin indium sulfide nanoribbons

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Indium sulfide is a widegap semiconductor material which could be an ideal candidate for various opto-electronic applications. We report the synthesis of indium sulfide nanoribbons from molecular precursors using a simple and fast solvothermal method. Depending on the experimental conditions, we obtain 2D colloidal nano-objects whose geometry varies from hexagonal nanoplates (Fig. 1.a) to long nanoribbons (Fig. 1.b). A very fine control of the lateral extension is achieved using a single experimental parameter.

The dimensions of these nano-objects are determined by TEM: the nanoribbons are 8 nm in width, 0.8 nm in thickness and several micrometers in length (Fig. 1.c.). High resolution dark field STEM enables the atomic scale characterization of these objects and highlights their crystallographic structure, which is also investigated by X-Ray diffraction. Furthermore, UV-visible spectroscopy is used to determine their optical absorption.

In order to study the formation mechanism of the nanoribbons we used time-resolved in situ synchrotron SAXS/WAXS.

Finally, we show we can control the bundling of the as-synthesized nanoribbons (Fig. 1.d) by the choice of the solvent of dispersion. Achieving stable colloidal solution of non-bundled nanoribbons is of a great importance in the perspective of obtaining liquid crystals, as we notice birefringence in non-bundled nanoribbons samples.

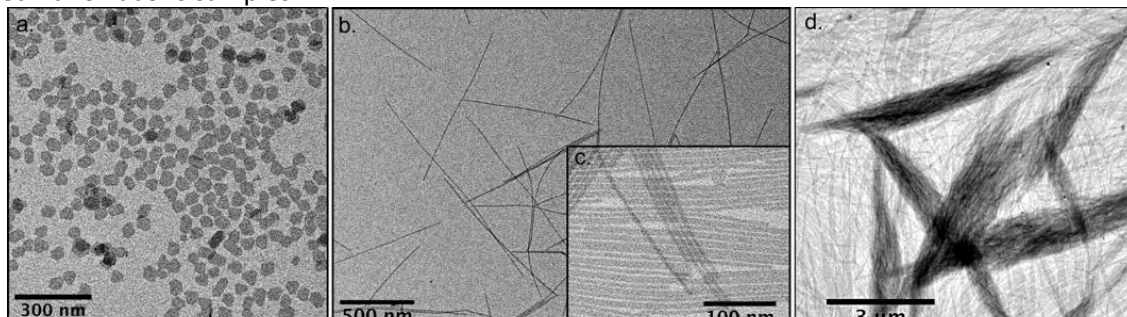


Figure 1. TEM images of indium sulfide hexagonal nanoplates (a.), nanoribbons (b., c.) and bundles of nanoribbons (d.).

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Thematic Session: Nanochemistry & nanoparticles

Keywords: Synthesis, Surface Chemistry, Nanocrystal, NMR

Controlling the Synthesis of InP Nanocrystals using the Secondary Coordination Sphere

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Abstract:

Indium phosphide quantum dots, InP QDs, are an important class of low toxicity QDs with great potential in optoelectronic (LEDs), catalytic (water splitting), and biomedical (cell imaging) fields.[1] InP QDs should be competitive with the more commonly encountered Cd and Pb chalcogenide QDs as they potentially have a wide emission range (470 nm – 918 nm), with narrow linewidths (< 40 nm). Experimentally, InP QD emission tunability and linewidth are limited and broad, respectively. These differences are linked to challenges in synthesizing monodisperse InP QDs, whereby the high temperatures and reactive precursors used, make QD growth difficult to control. To fully unlock the competitive properties of InP QDs their synthesis requires a fresh perspective. Here, I will discuss our new synthetic approach for InP. Our synthesis is based on a novel indium precursor, Indium (III) tris (N, N' – diisopropylacetamidinato), indium (III) amidinate.[2] Indium (III) amidinate allows the synthesis of monodisperse, oxide-free, InP QDs at temperatures as low as 90 °C. A high degree of optical tunability is achieved (absorbance and emission max) with competitive linewidths and quantum yields. The role of the precursor chemistry will be emphasized and in particular the importance of the second coordination sphere on the controlled growth of InP QDs will be demonstrated.

References:

- [1] B. Chen, D. Li, and F. Wang, *Small* 16, 2002454 (2020).
- [2] E. A. Baquero, H. Virieux, R. A. Swain, A. Gillet, A. Cros-Gagneux, Y. Coppel, B. Chaudret, C. Nayral, and F. Delpech, *Chem. Mater.* 29, 9623 (2017).

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Iron oxide nanoparticles, coprecipitation, microwave, superparamagnetism

One-step microwave synthesis of functionalized magnetic nanoparticles

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Functionalized superparamagnetic iron oxide nanoparticles have been synthesized according to a one-step process with the aim to produce stable water-dispersible nanoparticles with a well-crystallized spinel structure. Microwave technology is implemented here to fulfill this objective considering method's ease, speed and reproducibility¹. Several parameters have been modified and optimized (temperature, synthesis time, stirring, ratio molar between iron and ligands, volume of basis, power of microwave). The obtained nanoparticles are characterized by TEM, DLS, XRD, FTIR, TGA and magnetic measurements to understand the relations between the size, the shape, the composition and the magnetic properties. The functionalization efficiency (by citrate in standard conditions) is demonstrated using several complementary techniques. This functionalization *in-situ* is showing that is the main element to obtain nanoparticles without aggregation and stable in water. Magnetic measurements indicate the superparamagnetic behavior of nanoparticles with high saturation magnetization. The properties of stable water-dispersible iron oxide nanoparticles combined with the potential for use and modification of functionalized layer make these hybrid systems, developed in one-step in water, prime candidates for future healthcare and environmental applications.

(1) Venturini, P.; Fleutot, S.; Cleymand, F.; Hauet, T.; Dupin, J.; Ghanbaja, J.; Martinez, H.; Robin, J.; Lapinte, V. Facile One-Step Synthesis of Polyoxazoline-Coated Iron Oxide Nanoparticles. *ChemistrySelect* **2018**, 3 (42), 11898–11901.

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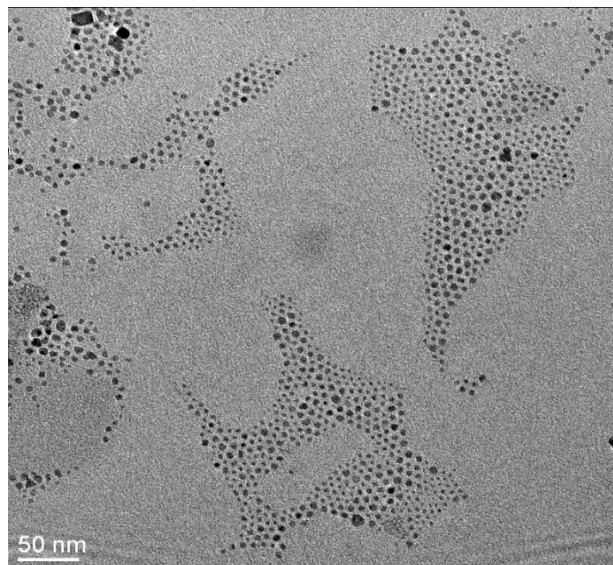


Figure 1: Micrograph TEM of iron oxide nanoparticles obtained via the microwave heating



Wednesday, November 24th

Session Nanochemistry & Nanoparticles

16:00 – 18:20

Abstracts

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Colloidal Stability, Surface Chemistry, Plasmonic Nanocrystals, Ligand exchange

Ligand Chemistry and Aggregation kinetics of Cs:WO₃ Nanocrystals

Capucine Cleret de Langavant^{1,2}, Yannis Cheref¹, Louise Daugas¹, Alexandre Baron³, Virginie Ponsinet³, Frederic Mondiot², Thierry Gacoin¹, Jongwook Kim¹

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3. *Centre de Recherche Paul Pascal, CNRS, University of Bordeaux, Pessac, France*

Abstract (**no longer than 250 words** (or 18 lines max. incl. figure), Calibri 11, single line spacing, black)

Highly-doped semiconductor nanocrystals have been studied these past decades with interest to their modulable free carrier concentration generating a tunable Localized Surface Plasmon Resonance (LSPR) across the whole Infrared range. LSPR of cesium-doped tungsten oxide nanocrystals (Cs:WO₃) is centered in the near-infrared (NIR) covering the solar spectrum, which is thus promising for solar energy control.

We developed synthetic methods to tune the LSPR spectrum of the Cs:WO₃ nanocrystals by controlling both the internal structure (crystal phase) and the nanocrystals' size and morphology [1]. Because the coupling effect of LSPR is subject to the particle's aggregation [2] maintaining the colloidal stability is essential to preserve the targeted optical properties for applications. Meanwhile, the optical spectroscopy is a quantitative tool to measure the aggregation state of the nanocrystals.

We have found that the colloidal stability of tungsten oxide family is particularly sensitive to the surface chemistry and ligand species of the nanocrystals. Oleic acid native ligands are very reactive even with small amount of protonic antisolvent, causing irreversible aggregation. In the same time, oleic acid desorbs easily from Cs:WO₃ surface during dilution or repeated centrifugation cycles, resulting in aggregation overtime and a significant loss of absorption cross section coefficient from $3.5 \times 10^{-14} \text{ cm}^2$ to $0.8 \times 10^{-14} \text{ cm}^2$. The higher the nanocrystal concentration is, the faster the nanoparticle aggregation occurs. After ligand exchange with Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DMOAP), the nanocrystal suspension remains highly stable over long time even at very high particle concentration enabling deposition of dense thin films.

References (max. 5):

[1] J-W Kim and all. "The interplay of shape and crystalline anisotropies in plasmonic semiconductor nanocrystals." *Nano Letters*, 2016: 3879-3884. [2] K-H Su and all. "Interparticle Coupling Effects on Plasmon Resonances of Nanogold Particles." *Nano Letters*, 2003: 1087-1090.

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Thematic Session: Nanochemistry & nanoparticles

Keywords: Nanocatalyst, oxides, CO₂ valorisation, heterogeneous catalysis

MgO nanocatalyst for the valorisation of CO₂ in the cycloaddition to epoxides

Cyprien Poucin and Sophie Carenco

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During the past century, the intensification of human activities along with the use of fossil fuels as primary source of energy caused the CO₂ concentration in the atmosphere to drastically increase. Capture, sequestration, and valorisation of this greenhouse gas are of primary importance to achieve the zero net global emissions urged by the Intergovernmental Panel on Climate Change in their last reports.

Magnesium oxide nanoparticles are promising catalysts thanks to the natural affinity of alkaline earth-oxides with CO₂ (due to the presence of both acid and basic site on their surfaces), to the availability of magnesium (one of the most abundant element on earth) and to the low hazard nature of magnesium oxide. By adapting a procedure reported elsewhere¹, we obtained nano-sized MgO, with an average crystallite size of 12 nm, by precipitation of Mg(NO₃)₂ salt in basic aqueous conditions followed by calcination at 500 °C. The catalyst was used in the cycloaddition of CO₂ to 2,3-epoxypropylbenzene to form the corresponding cyclic carbonate (4-benzyl-1,3-dioxolan-2-one) under 5 bars of CO₂, at 150°C and without solvent. This reaction limits the produced waste: the heterogeneous catalyst can be easily isolated and recycled by thermal treatment, cycloadditions produce a pure product and no solvent is required.

We have here the first blocks of a valorisation pathway for CO₂ respecting the general principles of green chemistry. Optimisation is now necessary to show that this kind of reaction can be economically viable.

Reference:

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Thematic Session: Nanochemistry and Nanoparticles

Keywords: Si-based particles, supercritical solvents, forward light scattering, metamaterials

Preparation of particles in supercritical conditions; interesting insights in the use of supercritical solvents in particles synthesis for optical applications

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Forward light scattering is a property where light is transmitted forward with no reflection in the backward direction, a property useful in light harvesting. Metamaterials with such properties can be created out of assemblies of particles. Silicon-based particles are excellent candidates for forward scatterers thanks to Si high refractive index and low absorption coefficient at optical frequencies. The particles should be smaller than the wavelength of incident light and large enough to support Mie resonances at optical frequencies, ideally between 100-200 nm in diameter. Moreover, to achieve efficient light scattering, the particles within the material should be the same size and composed of crystalline silicon. Recently, our team published a work reviewing the main methods of Si-based particles synthesis for optical metamaterials, highlighting their respective limitations and giving direction towards the most promising routes.(1) In our quest to create monodisperse, crystalline silicon particles, we developed a route to core-shell silicon@silicon oxynitride particles demonstrating higher scattering efficiency over a broader region of the visible spectrum than pure silicon particles.(2) These particles were obtained by combining a silicon coordination complex, bis(N,N'-diisopropylbutylamidinato)dichlorosilane, with trisilane in supercritical hexane. Decomposition of these two precursors led to a silicon core with a porous, nitrogen doped shell, that became oxidized upon exposure to air. By varying the ratio of the two precursors, the thickness of the shell was tunable. The optical properties depended highly on the sizes of the core and the shell, allowing forward scattering to be optimized. Theoretical simulations show that the magnetic dipole resonance is located in the core, where the electric dipole resonance is predominately in the shell.

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2. De Marco ML et al. Broadband Forward Light Scattering by Architectural Design of Core–Shell Silicon Particles. *Advanced Functional Materials.* 2021;31(26):2100915.

Acknowledgment:

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).

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: ZnSe, quantum dots, magic-sized cluster, one-pot synthesis, 1-dodecanethiol

Influence of thiol ligands on the ZnSe magic-sized cluster formation

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The unique optoelectronic properties of semiconductor nanocrystals, also termed quantum dots (QDs), have led to many advances in optoelectronic devices, bioimaging, and biosensing.¹ This strong potential in a wide range of applications sparked the interest for a better understanding of the QD formation mechanisms. Recent studies have shown that atomically defined, zero-dimensional magic-size clusters (MSCs) play a crucial role during the nucleation and growth of QDs. Thereby MSCs consist of discrete numbers of ions leading to narrow size distributions and thus narrow absorption peaks, which evolve in discrete steps from one stable size to the next.² The formation of MSCs was found in the synthesis of II-VI and III-V QDs but only limited synthesis approaches are available for the synthesis of MSCs in single-ensemble form without coexistence of other-size QDs.³

In this contribution, we present a synthesis strategy for the preparation of single-sized ZnSe MSCs. With a band gap of 2.7 eV and being an earth-abundant material, ZnSe QDs are interesting for light-emitting devices, blue-green lasers, photocatalysis, and as fluorescence probes. In contrast to other studies, our approach is based on a heat-up one-pot synthesis and uses less toxic and dangerous zinc precursors (e.g. zinc stearate). Knowing that thiol-based ligands can alter the formation process of ZnSe QDs, we investigated the influence of 1-dodecanethiol on the ZnSe MSC formation using absorption spectroscopy, TEM, XRD, SAXS, and MALDI-TOF MS. This study gives new insights into the complex interplay between precursors and ligands for the formation of MSCs.

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December, 8, 9 and 10



Thematic Session: Nanoparticles

Keywords: Nanoparticles, copper, well-defined size and shape, catalysis.

SYNTHESIS OF COPPER NANOPARTICLES WITH TUNABLE SIZES AND SHAPES

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During the last few decades, the metallic nanoparticles (NPs) are being widely studied due to their interesting physical properties (optical, electrical, thermal), which make them desirable for different applications in many fields, such as nanomedicine, catalysis and nanoelectronics.^[1] It is now well established that their shape and size play a very important role in determining their properties.^[2] It has also been shown that the morphology of various metallic NPs can be tuned through the control of the synthesis conditions and the nature of the ligands used. Among NPs of the 11th group, copper NPs has received less attention despite their lower cost compared to silver or gold due to their poor air-stability.^[3] The recent development of experimental approaches focus on the study of the morphologies and stability of copper nanoparticles.^[4] In this work, copper nanoparticles with controlled size distribution and well-defined morphologies are successfully synthesized from a simple disproportionation approach in the presence of different organic ligands. The mechanism of copper nanoparticles (CuNPs) formation was studied and found to strongly depend on the electronic and steric properties of the ligand used^[5].

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Magnetophoresis, cobalt nanorods, self-assembly

Synthesis of cobalt nanorods and self-assembly assisted by magnetophoresis

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The integration of performant sub-millimeter permanent magnets within electronic circuits remains a technological challenge. The classical approaches (sintering, mecnosynthesis) do not allow the shaping at the submillimeter scale while the thin film deposits do not reach sufficient thicknesses ($\approx 100\mu\text{m}$). The solution we develop relies on the self-assembly of cobalt nanorods by a magnetophoresis process. The final nanostructured magnet exhibits magnetic properties which result i) from the constituting nanorods and ii) from the assembly.

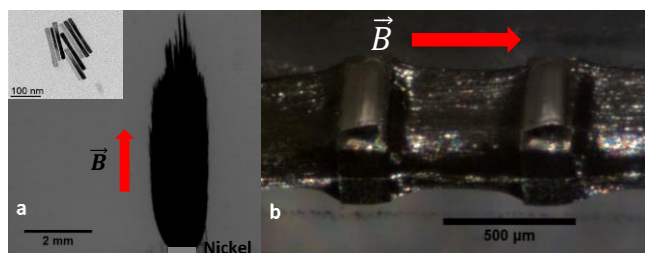


Figure 1 : a) perpendicular and b) planar magnetization. These magnets were prepared by controlled evaporation of a suspension of Co NRs (insert figure a)

The nanoparticles are synthesized by reduction of a carboxylate in a liquid polyol [1]. We developed an in-situ monitoring of temperature and H_2 emission during the synthesis to correlate the final morphology with the experimental conditions. We have shown that the premixing conditions were of primary importance to get well-defined Co nanorods. The nanorods are then dispersed in organic solvent using ultrasonic bath. The suspension is injected at the vicinity of nickel blocks placed under uniform magnetic field. The magnetic gradients induced by the blocks attract the nanorods: it's the magnetophoresis phenomenon (Figure 1). The assembly procedure involves the formation of macroscopic needles of Co NRs, their assembly by magnetophoresis and compaction during the drying. The understanding of the different phenomena is a key element to improve the structure of the final material (morphology and porosity). For this purpose, we developed a dedicated microscope set-up to observe in-situ the nanorods assembly. For that, an aluminum cell is placed under an optical microscope and the magnetic field is generating by an electromagnet. The evaporation of nanorods dispersion droplets under magnetic field is first used to assess and model the relative influences of magnetic and capillary forces. The full assembly process on Ni blocks is then studied, in planar and perpendicular geometries, in an aluminum cell placed in an electromagnet.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: eco-friendly process, bismuth, continuous flow, reproducibility

Eco-friendly Routes to Metallic Bismuth Nanoparticles

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The synthesis of nanoparticles is often regarded as wasteful, expensive and requires toxic reagents. This is particularly problematic when it comes to scale-up and in this context, the development of more environmentally friendly approaches is crucial. In this communication, we will present our latest results on the development of greener syntheses of metallic nanoparticles complying with the green nanochemistry principles.^[1] Our conditions are further optimized in continuous flow to increase productivity and enable larger scale production.

We demonstrate this methodology with the production of metallic bismuth (0) nanoparticles, which displays many important features such as a low cost, high biocompatibility and high X-rays absorption. These properties can be useful in a variety of applications such as in photochemistry, catalysis and in medicine such as in the development of new theranostic agents. In spite of these interests, no green synthesis of bismuth (0) nanoparticles has been described to date. Our study drastically reduces the amount of coating agents and uses only environmentally benign reagents. It compares the efficiency of two activation methods: microwave or thermal activations, both in terms of reproducibility and productivity.^[2] Our approach uses a newly designed continuous-flow device which connected downstream to an ultrafiltration device to obtain pure, stable and monodisperse nanoparticles.^[3]



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Thematic Session: nanochemistry & nanoparticles

Keywords: liquid phase synthesis, inorganic molten salts, perovskites, non-oxides, catalysis

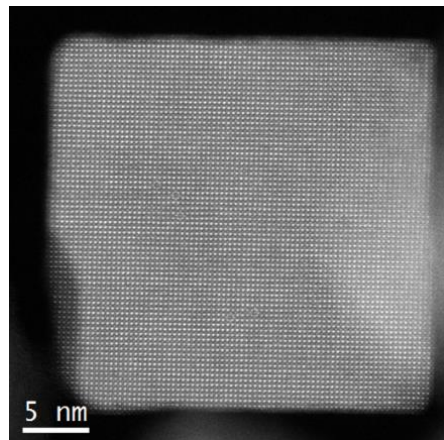
Original functional nanoparticles in molten salts

David Portehault¹, Ram Kumar,¹ Francisco Gonell,¹ Yang Song¹

1. Sorbonne Université, CNRS, Laboratoire Chimie de la Matière Condensée de Paris (LCMCP), 4 place Jussieu, 75005 Paris, France

The range of solids reported as nanoparticles is strikingly narrow compared to the library of bulk solids reported from conventional solid-state chemistry.[1] Many of these solids unreported at the nanoscale show properties without equivalent among more common phases often studied as nanoparticles, including ultrahardness, catalysis, magnetism, thermoelectric energy conversion or electrocatalysis. Because nanoscaling can modify, if not enhance, such properties, efforts to reach these still unreported nanoparticles are experiencing a burst. How to produce nanoparticles of solids typically obtained by solid-state reactions at high temperature? We will discuss our recent advances in the search of such challenging nano-objects by using inorganic molten salts as high temperature liquid media.[1–5] These liquids are thermally stable, possess large solvating ability, and fasten reactions compared to solid-state reactions. Such features enable triggering a wide range of reactions under kinetic control, thus leading to original nanostructures. We will start with nanoparticles showing properties different than those of bulk phases with perovskite oxide nanocrystals (see Figure) for spin transport[2] and electrocatalysis,[3] metal borides[4] and silicides [5] for catalysis and energy conversion. We will finally discuss the possibility to obtain genuinely new solids at the nanoscale, with the case study of a novel oxychloride solid and its photocatalytic properties for water splitting: $\text{Zn}_4\text{Si}_2\text{O}_7\text{Cl}_2$ nanowires.

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Thursday, November 25th

Session Nanochemistry & Nanoparticles

10:20 – 10:50 Keynote

Gaël DE PAEPE, CEA – IRIG, France

Abstracts

Keynote Speakers



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Biography

Gaël De Paëpe is currently leading the NMR-DNP group at IRIG (MEM, CEA/Univ. Grenoble Alpes). He obtained his M.Sc. and Ph.D. at ENS Lyon, France, under the supervision of Prof. L. Emsley. In 2004, he went to MIT for a postdoctoral work with Prof. R. G. Griffin. He returned to France in 2008 with an ANR Chair of Excellence to set up high-field NMR-DNP at CEA Grenoble. He received the Vold Memorial Prize (2013) and a consolidator grant funded by the European Research Council (2015). He is heading the Magnetic Resonance laboratory at IRIG-MEM since 2021. His group focuses on MAS-DNP method and technology development for applications in materials science, chemistry, and biology. More specifically, the NMR-DNP group is specialized in applications ranging from organic and inorganic NCs, energy materials to biomolecular systems (protein-ligand/ protein fibrils). The group is also a global leader in the development of new instrumentation and polarizing agents for MAS DNP at ultra-low temperature.

PROBING LIGAND COORDINATION IN ZINC OXIDE NANOCRYSTALS ENABLED BY DYNAMIC NUCLEAR POLARIZATION ENHANCED SOLID-STATE NMR

ZnO nanocrystals (NCs) have attracted significant research efforts owing to their versatility, with applications in numerous fields including catalysis, semiconductors, and in paint and rubber industries, as well as for their anti-microbial activity. Their shape, size, bulk composition (including the presence of dopant/vacancy), but also the ligand capping of these NCs determine their optoelectronic properties and their suitability for a particular application. Control over these parameters is a long-standing challenge, which implies establishing and optimizing new synthetic approaches. Nevertheless, the unambiguous characterization of the coordination chemistry of NC surfaces produced by wet-chemical synthesis remains a highly challenging issue.

In this presentation, we will show that Dynamic Nuclear Polarization combined with Magic Angle Spinning (MAS-DNP) can provide enough sensitivity to probe the ligand structure through multidimensional NMR experiments, which can be used to extract unprecedented information concerning ligand arrangements on NC surfaces.[1,2] First, we will highlight the vast difference between the organic-inorganic interfaces resulting from two synthetic routes to ZnO NCs capped with organophosphorous ligands: a traditional sol-gel approach and an organometallic approach called OSSOM (One-pot Self-Supporting OrganoMetallic).¹ MAS-DNP-enhanced NMR not only supplies a detailed NC surface analysis but also demonstrates the interest of the OSSOM approach for the preparation of highly stable quantum sized ZnO spherical nanocrystals. We will further discuss how MAS-DNP NMR can be used to determine ligand coordination modes and atomic-scale arrangements on faceted hexagonal ZnO nanoplatelets obtained through an organometallic approach.[2] Overall, this work relating ligand-binding modes with particle morphology will contribute to a rational design of tailored nanocrystals.

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Keywords: ZnO nanocrystals; dynamic Nuclear Polarization; solid-state NMR; ligand-NC interaction.

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December, 8, 9 and 10



Thematic Session: Nanophotonics & Nano-optics and Nanochemistry & Nanoparticles

Keywords: Silver nanocubes, dip-coating, controlled disorder, optical properties

Fabrication of metasurfaces by controlled disordered deposition of silver cubes

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Novel optical functionalities can be produced from artificial materials and 2D surfaces by controlling the morphology, composition and spatial arrangement of optically resonant particles. For example, surfaces decorated with silver nanoparticles^[1] (*figure 1*) can be particularly interesting for steering light scattering in reflection and transmission in the visible range. In this communication, we will report on the fabrication and optical properties of colloidal metasurfaces with controlled structural disorder. Specially, we control disorder by adapting the chemistry of the dispersion and the physicochemical properties during the particles deposition by dip coating^[2]. First results obtained for silver nanocubes deposited on a silicon substrate will be shown making emphasis on how they can be exploited to manipulate the reflectance properties of the surface.

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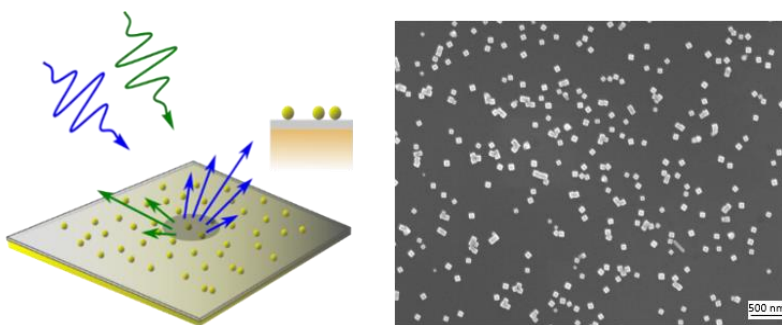


Figure 1: Diagram of a complex nanostructured surface (left) and SEM image of silver nanocubes deposited on a silicon substrate (right).

Acknowledgment: Funding ANR 'nano-appearance' #ANR-19-CE09-0014-01.

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Thematic Session: Nanochimie et nanoparticules

Keywords: Ag@TiO₂ NPs, catalysis, plasmonic, SERS, XANES, EXAFS

Plasmonic hybrid nanoparticles in catalysis

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Metallic nanoparticles (NPs) have many useful properties, in particular some NPs have unique optical qualities while interacting with light known as surface plasmon resonance (SPR).^[1] Plasmon excitation leads to a range of effects on molecule adsorbed or bound or in proximity to a NP such as thermal effects or charge transfer. The purpose of this study was to use the SPR phenomenon for accelerating catalytic reaction rates under laser irradiation using a well-designed catalyst bound to metallic NPs. The core-shell NPs were classically synthesized and the resulting Ag@TiO₂ NPs have been functionalized by a 2,2'-bipyridine-based ligand (L) bearing a phosphonic acid tether to ensure an ionic-covalent anchoring onto TiO₂ to form Ag@TiO₂@L. In the last step, copper(I) or copper(II) salts reacted with Ag@TiO₂@L to form Ag@TiO₂@L-Cu nanocomposites. Copper was chosen because it is an earth-abundant metal, making its use more cost effective and more sustainable than precious transition metal catalysts.

The resulting new nanocomposites were characterized by UV-vis, TEM-EDX. Then, the efficiency of these nanocomposites was investigated under laser irradiation and the Ullmann reaction was chosen as a model reaction.^[2] The hybrid nanocomposites were proven to be efficient in accelerating the rate of the latter reaction under light irradiation.^[3,4] To further characterize those nanomaterials, we performed SERS and XAS spectroscopy on both copper(I) and copper(II) hybrid materials.^[5] To propose a mechanism, future work will be directed to combine operando XAS/Raman investigation of copper and its environment during catalysis. It should allow us to monitor oxidation state of copper under laser irradiation and record at the same time RAMAN spectra to monitor the ligand's structure evolution.

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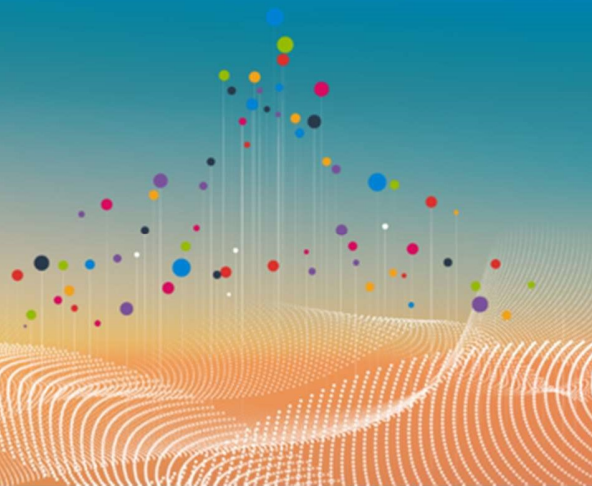
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Thematic Session: Nanochemistry & Nanoparticles

Keywords: biomass, furfural, 5-hydromethyl furfural, bimetallic, nanoparticles, theoretical calculations

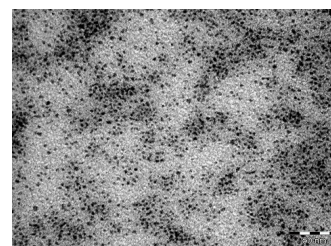
Upgrading biomass by bimetallic catalysts

Miquel Cardona¹, Pierre Lecante², Chiara Dinoi³, Iker del Rosal³, Romuald Poteau³, Karine Philippot¹, M. Rosa Axet¹

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2. Centre d'élaboration des matériaux et d'études structurales UPR CNRS 8011, 29 Rue Jeanne-Marvig, BP 4347, 31055 Toulouse, France
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Converting lignocellulosic biomass into sustainable chemicals and fuels is of major interest to reduce dependence on fossil fuel sources. Ideally, liquid fuels would be made from second generation feedstocks compatible with current combustion engines, and chemically identical to those obtained from petroleum. A promising feedstock is lignocellulosic biomass, which contains cellulose, hemicellulose, and lignin, and is abundant in the form of agricultural residues, waste streams, wood, and energy crops. It is also of interest to replace petroleum derived chemicals with similar products derived from biomass, as chemicals from renewable sources can reduce the environmental impact.

From lignocellulosic biomass, furfural and 5-hydroxymethylfurfural (HMF), two platform molecules, can be produced. By the reduction of HMF, 2,5-dimethylfuran, a potential biofuel, and 2,5-dihydroxymethylfuran, an interesting symmetric molecule, are obtained selectively using metallic catalysts. The incorporation of a second metal changes the properties of the metal nanoparticles (NP) surface, with respect to their monometallic counterparts, regarding geometric and electronic effects, which can have a positive effect on selectivity. We present here the synthesis and application in catalysis of RuNi NP. The NP



TEM image of RuNi nanoparticles stabilized with polyvinylpyrrolidone (scale bar 50 nm).

present a core-shell structure in which Ni is on the surface. This chemical order and by playing with Ru/Ni ratio allows to control the Ni coverage of the NP. Their catalytic behavior in the selective hydrogenation of furfural and 5-hydroxymethylfurfural points out to a synergetic effect between both metals. Theoretical calculations performed onto a hydrogenated Ru NP surface are in line with the experimental results, and allow to shed light on the high selectivity found for Ru NP based catalyst. References: [1] Hu, L.; Xu, J.; Zhou, S.; He, A.; Tang, X.; Lin, L.; Xu, J.; Zhao, Y. Catalytic Advances in the Production and Application of Biomass-Derived 2,5-Dihydroxymethylfuran. *ACS Catal.* **2018**, *8*, 2959-2980, [2] Dhanda, R.; Kidwai, M. Graphene Supported RuNi Alloy Nanoparticles as Highly Efficient and Durable Catalyst for Hydrolytic Dehydrogenation-Hydrogenation Reactions. *ChemistrySelect* 2017, *2*, 335-341. Acknowledgment: This work was supported by the CNRS, MESRI and Calcul en Midi-Pyrénées.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: flow chemistry, rapid mixing, nanodisks, co-reduction, polymers

Flow synthesis of silver nanodisks: mechanisms & rational processing

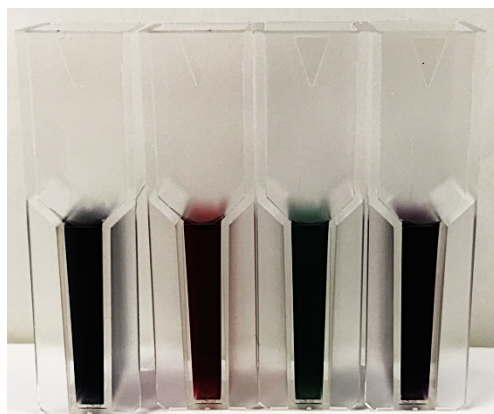
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Abstract:

Like most anisotropic nanoparticles, silver nanoparticles may be synthesized via rather complex wet chemistry routes. However, both control and reproducibility remain challenging, which also results in a limited mechanistic understanding on how these structures form. Our hypothesis is that the interplay of thermodynamic and kinetic factors is far too complex to be adequately mastered in standard, but usual, batch preparation methods.

We have thus designed a continuous flow setup, based on millifluidic vortex mixers, able to simultaneously deliver a millisecond time-resolution and high fluxes. This setup is therefore compatible with both fine mechanistic studies and industrial scale-up. We tested this tool on the complex and sensitive synthesis of silver nanodisks, which are formed through a co-reduction method in the presence of a stabilizer such as PVP. As illustrated in the picture below, simple modifications of the reaction pathways, achieving the exact same final composition, are sufficient to yield different nanostructures. We succeeded in uncoupling the contributions of each species in the formation of these nanodisks, which yields rational formulation guidelines to obtain these structures. A perfect reproducibility was achieved with the setup, yielding indiscernible dispersions cycle after cycle.



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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Gold nanoparticles, in-situ synchrotron studies, non-classical nucleation, pre-nucleation clusters.

The role of pre-nucleation clusters in the crystallization of gold nanoparticles

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Synthesizing gold nanoparticles with different nanostructures (morphology: ultrasmall nanospheres (NSs) and nanowires (NWs); crystallinity: icosahedral and tcp structure) [1] are pivotal for various applications including catalysis, sensors and drug delivery. Generally, the relation between synthetic parameters and final morphology of nanoparticles are well established by empirical approach. However, the complete description to achieve unique gold nanostructures was ill-documented. Until recent times, formation of gold nanoparticles in solution is described by classical nucleation theory (CNT) [2] or by LaMer's model. Nevertheless, the recent evidences suggest that there are other pathways exist i.e. non-classical process: from ions to nanoparticles via one or several transient, amorphous intermediate states (pre-nucleation clusters (PNCs), amorphous nanoparticles, etc.) instead of crystalline nuclei. To understand the growth mechanism, in-situ synthesis of gold NSs/NWs in hexane were followed, from few seconds to several hours, using a mixing device in coupling with synchrotron X-ray techniques (small angle X-ray scattering, X-ray absorption spectroscopy and high energy-X-ray diffraction). With these experiments, we show that both gold NSs and NWs are evolved via PNCs of size ca. 3-4 nm. Further, we propose that the active PNCs are responsible for nucleation while non-reactive PNCs acting as reservoir for further growth process. Therefore, from this study, we conclude [3] that the size and the reactivity of PNCs are determining factors in controlling the final morphology of gold NSs/NWs instead by concentration of Au species and temperature, as predicted by CNT.

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2. B. Abécassis et. al., *Nano Lett.* 7, 1723-1727 (2007)
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Acknowledgment: RKR acknowledges Fédération FERMAT (Université de Toulouse) for financial support during his post-doctoral stint. We thank SOLEIL (France) and PSI (Switzerland) synchrotron facilities.



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The Nanoscience Meeting

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Centre des congrès Pierre Baudis

December, 8, 9 and 10



Thematic Session: Nanochemistry & Nanoparticles

Keywords: electrodeposition, nucleation/growth, dendrites, shape stability, space charge

Metal nanostructures formed by electrodeposition in microchannels: study of the growth mechanism and application to SERS

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The electrodeposition of a metal is known to be able to lead to the formation of metal *ramified structures* (RS) which are commonly called *dendrites*. Under particular conditions (Hele-Shaw/thin gap cell and no supporting electrolyte), RS exhibit a small structure which consists of metal nanocrystals [1]. The two interesting aspects of this electrochemical formation of nanostructures are 1) the in situ formation and 2) the immobilization inside the cell. The use of microfluidic connections then allows both the required purification of the nanostructure by flushing and the controlled injection of reagents/solutes [2]. This can be advantageously implemented, by the use of the deposited nanostructure as Surface Enhanced Raman Spectroscopy (SERS) substrate, for flow chemistry applications (chemical imaging).

Since the SERS signal strongly depends on nanostructure properties, how the size and shape of nanocrystals depend on the electrodeposition conditions (current density j and metal salt concentration) is studied. For Cu and Ag, SEM imaging shows a morphological transition of the nanocrystals: below a critical current density, the nanocrystals are non-dendritic (equilibrium shape) while above they are dendritic. The RS formation is ensured by a nucleation/growth (re-nucleation) regime at low j [1] and only by growth (without re-nucleation, dendrite=single crystal) at high j . It is shown that the theoretical description of this transition (by a Mullins & Sekerka shape stability analysis) requires taking into account of the deviation from electroneutrality through a space charge layer. In situ formed RS, made of Ag nanodendrites, showed an enhancement of the Raman signal.

References:

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[2] A. Iranzo and F. Chauvet, Microfluidics and Nanofluidics 23, 45 (2019)



Thursday, November 25th

Session Nanochemistry & Nanoparticles

14:00 – 15:10

Abstracts

C'Nano 2020

The Nanoscience Meeting

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December, 8, 9 and 10



Thematic Session: Nanochemistry & Nanoparticles

Keywords: inorganic nanoparticles; structural characterization; nucleation & growth mechanisms

40 years of PDF in Toulouse

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To validate structure-properties relationship, structural characterization is of course needed. Also to improve simulations through more realistic parameters. Also to guide original syntheses and save time and resources. At the nanoscale, PDF is recognized as one of the few techniques providing safe and accurate information.

Toulouse belongs to a quite select club: since more than 40 years, PDF studies are routinely done in-lab using local resources [1], usually in combination with TEM. Originally dedicated to the structural study of inorganic glasses [2] and molecular complexes [3], its full potential appeared with the nano-revolution [4]. Both TEM and PDF improved with time, allowing to investigate always more complex nanomaterials. However, PDF does not only provide accurate insight of order and disorder (structural or chemical, local or extended), but being a statistic technique just like classic XRD, it helps putting TEM results in perspective and may avoid pitfalls.

A selection of studies on nanoparticles elaborated by wet chemistry will be presented to illustrate the capacity to solve, and often detect, unexpected structural issues: size effects, ligand effects, segregation vs. alloying...

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1. LASIP - A Liquid And Amorphous Structure Investigation Package, Lecante P., Mosset A., Galy J.; *J. Appl. Cryst.* (1985), DOI: 10.1107/S0021889885010172
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Thematic Session: (Nanochemistry & nanoparticles)

Keywords: (nanoparticles, nanometrology, SAXS, in-situ)

Synthesis of SiO₂ Nanoparticles as reference materials : metrology measurements and in situ kinetics in lab by Small angle –X-ray scattering

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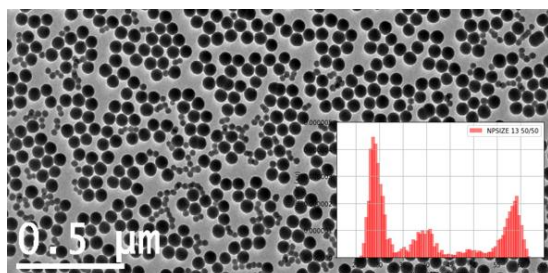
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The unambiguous correlation of possible health and sustainability risks to nanoparticle size must be enabled by reliable measurement of nanoparticle size, to ensure comparability and compatibility between results measured under different methods. The NPSIZE project funded by European Metrology Program (EMPIR) develop methods, reference materials and modelling to improve the traceability chain, comparability and compatibility of nanoparticle size measurements.

In this work, we present how spherical silica nanoparticles are synthesized with controlled monomodal or bimodal dispersion to be use as reference materials and international round-robin.

Improving the fabrication requires a fine understanding of synthesis (1), coupled with an expertise of in-situ or ex-situ analysis methods. This is a new challenge for the analysis : determining not only average characteristics (size, chemical composition and shape ...) but also the concentration and the distribution over the population studied (2).

Small-Angle X-ray Scattering (3) allows very precise measurements of the nanoparticles size and concentration that can be directly link to the metric system (4) (metrological traceability) . We developed a SAXS laboratory instrument dedicated to the in-situ characterization of nanoparticles, which enable fast measurements, and the monitoring of the synthesis parameters. Measurement protocols and software processing chain (5) (i.e. size distribution) are also combined & optimized.



TEM images with SAXS estimated dispersion of 50% 30nm and 50% 60nm spherical silica nanoparticles



Samples dispersions ready to be shipped to partners for metrology measurements

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Acknowledgment: This project receives funding from the European Metrology Programme for Innovation and Research (EMPIR) which is an integrated part of Horizon 2020, the EU Framework Programme for Research and Innovation.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: quantum dots, surface functionalization, fluorescence, vibrational spectroscopy

Self-assembled monolayers of CdTe quantum dots: chemisorption versus physisorption

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At the interface between physics and chemistry, our work aims at the assembly of nanostructured platforms made of silica substrates, organic underlayers and colloidal CdTe quantum dots (QDs). Through this study, we demonstrate that the immobilization of such 3 nm-size nanoparticles can be achieved on common glass substrates thanks to a protocol much less complex than usual methods. Besides, by comparing two competitive assembly strategies respectively based on physisorption and chemisorption, we show that the former is the most efficient, contrary to all expectations [1]. By physisorption, the QDs keep their native optical properties [2]: the absorption and emission bands do not suffer from spectral shifts or broadenings. This surprising result stands in stark contrast to the literature, which systematically considers chemisorption as mandatory for the achievement of stable QD monolayers. As characterized by quantitative analyses performed through UV-Visible spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Fluorescence Microscopy, Time-Resolved Fluorescence spectroscopy, and Two-Color Sum-Frequency Generation spectroscopy (2C-SFG), our 2D-monolayers of QDs are dense, homogeneous, stable over time, reproducible and optically coupled to their molecular environment. Thanks to the use of the unconventional technique of 2C-SFG, a nonlinear vibrational spectroscopy combining two input IR and visible laser beams [3], a vibroelectronic coupling between the QDs and the organic underlayer is indeed observed: when the QD layer is excited by visible light, it enhances the IR vibrational response of the underlying molecules deposited on the platform.

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[1] J. Hottechamps, T. Noblet, C. Humbert, L. Dreesen et al. *ChemPhysChem* **21**, 853 (2020)

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Thematic Session: Nanoparticles

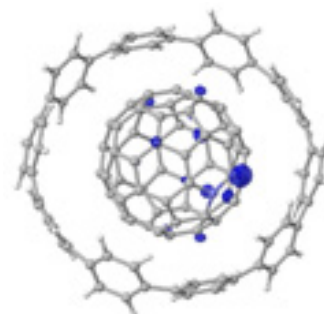
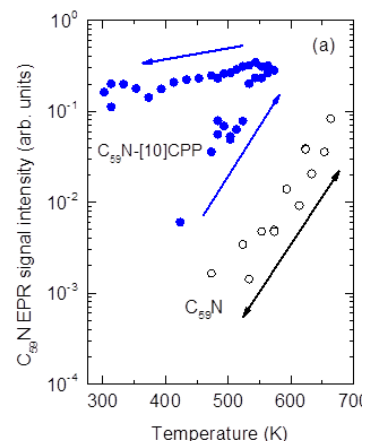
Keywords: carbon, fullerenes, azafullerenes, spin, cycloparaphenylenes, bottom-up, DFT

Bottom-up design and realisation of stable fullerene spin systems

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Discrete energy levels of quantum spins at the molecular level are a promising platform for realising qubits. The major challenge remains how to build complex circuits from such molecular spin entities with sufficiently long decoherence times in order to conduct quantum computation algorithms. A major handicap towards exploitation of radicals is their inherently instability. In paramagnetic azafullerenyl radical $C_{59}N\bullet$ the unpaired electron is strongly localized neighbouring the nitrogen and induces dimerization to diamagnetic bisazafullerene $(C_{59}N)_2$. We develop an innovative radical shielding approach using supramolecular complexation, exploiting the protection offered by a [10]cycloparaphenylene ([10]CPP) nanobelt ('the shortest carbon nanotube') encircling the $C_{59}N\bullet$. Photo-induced radical generation is increased 300 times. The characteristic triplet signal of $C_{59}N\bullet@[10]CPP$ is traced even after several weeks, a lifetime increase of $>10^8$, and in the solid phase produced via thermolysis, currently for several years. This talk will focus on the role of DFT calculations in guiding this nanocarbon molecular design, and explore future possibilities for bottom-up design in fullerenes and ultra-short nanotubes.



References: See www.ewels.info for full list.

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We acknowledge regional "Pari Scientifique" funding NEWTUBE for financial support.

