



Poster Session

Book of abstracts



P1 - Nano-Optics & Nanophotonics

C'Nano 2020

The Nanoscience Meeting

TOULOUSE

Centre des congrès Pierre Baudis

December, 8, 9 and 10



Thematic Session: Nanophotonics & nano-optics

Keywords: Photonic crystals, self-collimation, mesoscopic systems, modelling

Efficient design of mesoscopic self-collimating photonic crystals

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Mesoscopic photonic crystal (M-PhC) is a macroscopic periodic structure, alternating slabs of photonic crystals (PhC) and slabs of homogeneous material (bulk). Theoretical and numerical studies show that they can combine PhC guiding properties (such as self-collimation, SC) [4] and controlled reflectivity from the alternation of slabs (DBR-like structure) [1] [3]; opening the path to a complete new family of photonic structures [2]. Unfortunately, M-PhC depends on many more parameters than simple PhC, such as: PhC slab size (d_c), bulk size (d_b), in addition to the PhC classic parameters (hole radius, period, optical index). A parametric study of M-PhC using traditional methods like FDTD or RCWA is thus highly impractical.

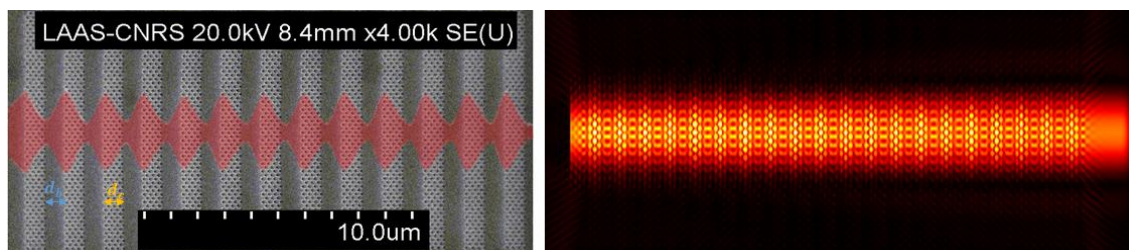


Fig 1. Left: Scanning electron microscope image of M-PhC ensuring MSC/AR. In red, MSC artistic view. Right: Electromagnetic field propagation inside a MSC/AR structure, FDTD simulation

Previous approaches [1] concentrated on achieving mesoscopic self-collimation (MSC) and on selecting structures presenting good antireflection (AR) or high-reflection (HR) properties. We present a novel approach that allows a complete parametric study of the design of such structures, without relying on time-consuming simulations. We show that, concentrating first on the reflection properties of the M-PhC and then its M-SC properties, a fast parametric algorithm can be define that enables direct design of a full high-reflection or anti-reflection MSC structure. Simulations, to verify the structure's properties [Fig 1], were performed with the open-source finite-difference time-domain (FDTD) method [5].

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Thematic Session: Nanophotonics & nano-optics

Keywords: nanoparticles, plasmonics, ultrashort laser pulse, electron emission, near field dynamics

Ultrafast dynamics of the near-field topography around gold nanoparticles

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When a noble metal nanoparticle (NP) is exposed to an ultrashort laser pulse tuned to its localized surface plasmon resonance, a large amount of light energy is absorbed, resulting in a series of ultrafast events. Thus, electron emission from the NPs to their surrounding environment occurs, inducing in a biological medium the generation of free radicals (reactive oxygen species, or ROS) capable of destroying cancer cells [1,2]. This electron ejection is strongly influenced by the topography of the local electromagnetic field enhanced by the plasmon resonance [3].

The aim of this work is to determine the dynamics of the topography of the optical near-field throughout the duration of the laser pulse. This will allow us to deduce the spatial, temporal and energetic characteristics of the electronic emission in order to understand the formation of ROS. This could then help us for optimizing the latter for therapeutic applications.

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Acknowledgment:

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Thematic Session: Nanophotonics

Keywords: 1D photonic crystal, opto-mechanical oscillator, optical bistability, chaos

Coupled opto-mechanical oscillators on chip towards applications

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An increasing number of researches studying coupled resonator systems are motivated by the large number of possible applications and the interest of fundamental understanding. The study of such systems has the potential to investigate the optical nonlinear dynamics, frequency locking or oscillation phase-noise reduction. Nanofabricated one dimensional photonic crystals (Fig. 1.) can confine optical and mechanical modes in a high quality factor cavity, creating a nano-sized optomechanical oscillator. The mechanical motion is read by the optical field thanks to its coupling with the mechanical field. Converting this optical signal into the radiofrequency domain we observe the mechanical modes in the MHz and GHz range [1]. In our study we experimentally investigate the behavior of a coupled system containing an array of photonic crystals integrated on the same chip in order to couple them optically through a common waveguide. By coupling high optical powers into the cavities we observed bistability in the optical spectrums of the cavity resonances. A period-doubling of the MHz mechanical modes is also observed (Fig. 2) while these bistable cavity regimes are coupled together. This non-linear behavior is potentially leading to a chaotic behavior [2], widening the possible applications range of the optomechanical oscillators towards random number generation or chaotic encryption.

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Acknowledgment: This work is supported by the European Unions Horizon 2020 research innovation program under grant agreement No 732894 (FET Proactive HOT) and the Agence Nationale de la Recherche as part of the JCJ project ADOR (ANR-19-CE24-0011-01) and as part of the ASTRID program CRONOS (ANR-19-ASTR-00-22-01)

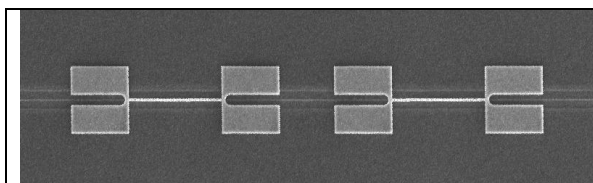


Figure 1.: Scanning electron microscope image of two one dimensional photonic crystal above a common optical waveguide

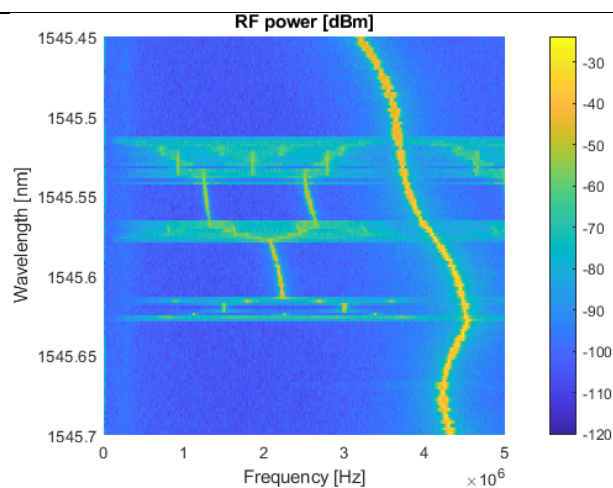


Figure 2: RF spectrogram of the MHz mechanical mode in the optical bistability wavelength range

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Thematic Session: Nanophotonics & Nano-optics.

Keywords: SERS, plasmons, optimization, multi-spectral substrate.

Gold Nanocylinders on Gold Film as a Multi-spectral SERS Substrate

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The surface enhanced Raman scattering (SERS) efficiency of gold nanocylinders deposited on gold thin film is studied. Exploiting the specific plasmonic properties of such substrates, we determine the influence of the nanocylinder diameter and the film thickness on the SERS signal at three different excitation wavelengths (532, 638 and 785 nm). We demonstrate that the highest signal is reached for the highest diameter of 250 nm due to coupling between the nanocylinders and for the lowest thickness (20 nm) as the excited plasmon is created at the interface between the gold and glass substrate. Moreover, even if we show that the highest SERS efficiency is obtained for an excitation wavelength of 638 nm, a large SERS signal can be obtained at all excitation wavelengths and on a wide spectral range. We demonstrate that it can be related with the nature of the plasmon (propagative plasmon excited through the nanocylinder grating) and with its angular dependence (tuning of the plasmon position with the excitation angle). Such an effect allows the excitation of plasmon on nearly the whole visible range, and paves the way to multispectral SERS substrates.

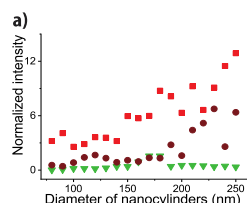


Figure 1: Evolution of the SERS intensities of the band located at 1580 cm^{-1} depending on the nanocylinder diameter and for the film thickness of 20 nm. The SERS intensities have been normalized by the silicon Raman signal. Green triangles: excitation wavelength of 532 nm; Red squares: excitation wavelength of 638 nm; Brown circles: excitation wavelength of 785 nm¹.

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Thematic Session: Nanophotonics & nano-optics

Keywords: CMOS Image Sensor, Near-infrared detection, Polysilicon Nanograting, Quantum Efficiency, Crosstalk

Design of a poly-silicon nano-grating for enhancing near-infrared detection of CMOS image sensors

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CMOS Image Sensor efficiency in the near-infrared (NIR) spectrum (starting at $\lambda=780$ nm, ending at 1100 nm due to the silicon bandgap) is limited by the absorption length in silicon. The junction depth is of a few microns whereas the absorption length is $12 \mu\text{m}$ for $\lambda=800$ nm, leading to a loss of photo-generated carriers in bulk recombination. To deal with that limitation we modeled NIR enhanced photodiode, considering a 180 nm standard CMOS process that does not require any modification in the process flow. We implemented nano-grating on top of the photodiode using the polysilicon layer [1]. The diffraction effect of the nano-grating increases the length of the optical path in the junction area, which allows more photocurrent to be collected before recombination [2]. Moreover, the nano-grating has an antireflection property that enhances the optical efficiency. Consequently, the External Quantum Efficiency (EQE), which is the ratio of the number of collected electrons to the number of incident photons, is enhanced. The drawback of the diffraction effect is the collection in adjacent pixels of the incident light, named crosstalk; however, grating together with Deep Trench Isolation (DTI) [3] could decrease crosstalk and increase EQE providing a resolution equal or better than that of the standard pixel and higher sensitivity. We coupled optical simulation, which calculates the number of photo-generated electrons, and electronic simulation, which calculates the probability of electron collection, using the software LUMERICAL [4]. We report a 15.1% EQE enhancement and a 8.5% crosstalk reduction at 800 nm.

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Thematic Session: (eg. Nanophotonics & nano-optics, nanomaterials, ...)

Keywords: photonics, rare earth, PLD, processing

Micro-emitters fabricated by Pulsed Laser Deposition liftoff processing in rare earth doped oxide layers

Alban Gassenq,¹ Etienne Cleyet-Merle,¹ Hoshang Sahib,¹ Stephan Guy,¹ Bruno Baguenard,¹ Frederic Lerouge,³ Ali Belarouci,² Régis Orobtcouk,² Sébastien Cueff,² Hai-Son Nguyen,² Yannick Guyot,¹ Antonio Peireira¹

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Rare earth emitters are promising in integrated optics but require complex integration (etching, bonding...). In this work, we have fabricated rare earth doped oxide micro-emitters without etching using an innovative fabrication method: the Pulsed Laser Deposition (PLD) based lift-off processing[1]. Lift-off processing is usual in microelectronics to avoid etching material but is limited to layers with low thermal budget. PLD overcomes such limitation since the atoms that reach the surface during deposition have a high kinetic energy that allows the growth of films on substrates in a range of temperatures much lower compared to other technics[2]. Therefore, the possibility to merge both technologies (i.e lift-off and PLD) is of great interest for the direct integration of crystalline photonics micro and nano-structures without etching. In this work, we have fabricated Er and Eu doped Al_2O_3 or Y_2O_3 microstructures by PLD based liftoff processing. High crystallinity and strong emission in the visible and Infra-Red (IR) wavelength ranges were first studied in planar $\sim 0.5\mu\text{m}$ layers. Different designs were then studied (diffraction grating, micro-strip, micro-disk...). Using such processing, enhancement of the light emission by diffraction and light confinement were demonstrated showing the high potential of PLD based liftoff processing to fabricate micro and nano-structures without etching.

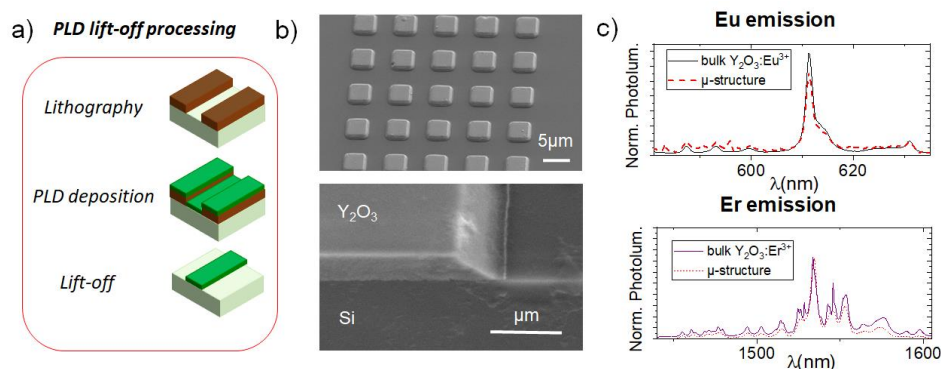


Figure 1 : a) PLD based liftoff processing; b) examples of fabricated microstructures and c) photoluminescence measurements for Er and Eu doped Y_2O_3 microstructures

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Thematic Session: Nanophotonics & nano-optics.

Keywords: Non-linear microscopy, two-photon fluorescence imaging, single-particle tracking, particle size characterization, free diffusion.

Single-Particle Tracking with Scanning Non-Linear Microscopy

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Abstract

This study describes the adaptation of non-linear microscopy for single-particle tracking (SPT), a method commonly used in biology with single-photon fluorescence. Imaging moving objects with non-linear microscopy raises difficulties due to the scanning process of the acquisitions. The interest of the study is based on the balance between all the experimental parameters (objective, resolution, frame rate) which need to be optimized to record long trajectories with the best accuracy and frame rate. To evaluate the performance of the setup for SPT, several basic estimation methods are used and adapted to the new detection process. The covariance-based estimator (CVE) seems to be the best way to evaluate the diffusion coefficient from trajectories using the specific factors of motion blur and localization error.

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Acknowledgment: This work was partially funded by ANR under Project ANR-17-CE09-0009 SIPAIE (Aggregation Induced Emission at Single Particle level).



P2 - 1D & 2D NANOMATERIALS

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POSTPONED



**NEW
DATES**

**November
23, 24, 25
2021**

Thematic Session: 1D & 2D Nanomaterials

Keywords: ZnO nanowires, MOCVD growth, AFM, mechanical properties

Growth and mechanical properties mapping of ZnO nanowires

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Abstract

ZnO nanowires were fabricated using MOCVD (metalorganic chemical vapor deposition) technique on different substrates, namely sapphire, silicon, AlN/Si, and GaN/AlN/Si. Selective area growth (SAG) has also been investigated using SiN/sapphire patterned substrates. In this latter case, the growth of the nanowires is initiated from a geometric array of holes made into the dielectric mask of SiN, which was previously fabricated using electron beam nanolithography. The goal is to achieve vertical ZnO nanowires with a perfect crystal quality.

Then, the nanowires grown on silicon were embedded in a polymer (PMMA) or spin-on glass (SOG) matrix, and subsequently polished to elaborate suitable samples for the AFM characterization. Mechanical properties mappings clearly show the individual nanowires. A model for the indentation process is developed and allows to extract the Young's modulus value of the ZnO nanowires.

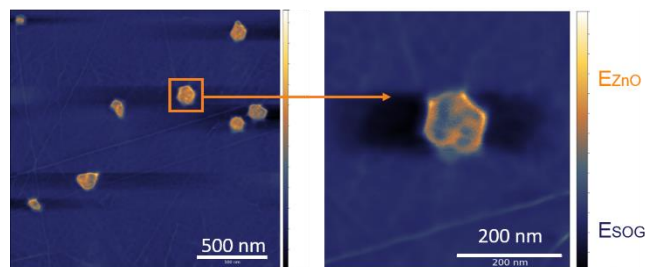


Figure : Young's modulus mapping of ZnO nanowires embedded in spin-on-glass (SOG) matrix

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Thematic Session: Nano-optics, nanomaterials.

Keywords: Sol gel method, Nanoparticles, Perovskite, Optical property, FTIR spectroscopy.

Study of Nanostructural, morphologic, and Optical properties for nanocrystalline $\text{La}_{1-x}\text{Bi}_x\text{Ni}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($x=0.0, x=0.2$).

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Abstract

Perovskite-type oxides $\text{La}_{1-x}\text{Bi}_x\text{Ni}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($x = 0.0-0.2$) were prepared by the sol-gel method. A thermal characterization technique was used to obtain the optimal formation temperature for the sample. In this part, we study the TGA thermogravimetric curves and the typical DSC calorimetric analysis obtained for the burnt powder. X-ray diffractogram and sound Rietveld's refinement confirms the formation of the Perovskite structure. Our samples are single-phase and crystallize in the orthorhombic system with the space group Pnma. Morphology analyzed by transmission electron microscopy shows that the grain is composed of different crystallites, on the other hand analyzed by scanning electron microscopy shows an agglomeration of our samples. The composition and purity of the samples were investigated using EDXS. The FTIR spectra confirmed the formation of the structure of orthorhombic perovskite. UV-visible spectroscopy is used to analyze the absorption of materials and determine gap energy.

Thematic session: 1D Nanomaterials.

Keywords: Electrodeposition, tellurium, nanostructures, thermoelectricity.

Electrodeposition of Te nanostructures

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Abstract

The conversion of heat into electricity and vice versa while minimizing energy losses corresponds to the principle of thermoelectricity. The best thermoelectric materials present minimum thermal conductivity associated with maximum electrical conductivity and Seebeck coefficient. Nanostructuring can be a solution to improve thermoelectric performances despite these opposite properties, as lattice part of the thermal conductivity can be independently lowered when moving from bulk to nanostructures [1,2].

Among the thermoelectric materials, Tellurium has a high Seebeck coefficient ($500\mu\text{V}\cdot\text{K}^{-1}$) at room temperature but a high thermal conductivity ($3\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$). In this work, we synthesized self-standing Te nanostructures by electrodeposition technique, taking advantage of the templating properties of ionic liquids solvents (IL). Single crystalline nanostructures were systematically obtained with a preferential orientation along the [001] direction. By varying the conditions of electrodeposition, shape and size of nanostructures can be tuned: nanorods, nanowires and nanotubes were synthesized, with diameters that can be lowered to 50 nm. Nanostructures aspect ratio depends on the overvoltage and nanotubes can be obtained in high overpotential conditions due to mass transport effects. By changing the composition of the IL electrolyte, the speciation of Te^{IV} can be modulated and hair-like nanowires of $70\mu\text{m}$ long and $50\pm 20\text{nm}$ in diameter can be synthesized [2,3]. Finally, small rods of $77\pm 13\text{nm}$ in diameter and less than $1\mu\text{m}$ long were grown by applying a small charge density. These nanostructures are of great interest to elaborate flexible hybrid organic/inorganic thermoelectric materials, combining nano-Te thermoelectric properties and high electric/low thermal conductivity of conducting polymers [4].

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Structural characterization, magnetic and magnetocaloric properties of $\text{Pr}_{0.8}\text{K}_{0.2}\text{MnO}_3$: A comparison between solid-solid state and sol-gel process

BENKHALIFA.J, CHAABANE.M

We have performed a systematic study of the critical properties of $\text{Pr}_{0.8}\text{K}_{0.2}\text{MnO}_3$ manganite synthesized using two various methods in the vicinity of the ferromagnetic–paramagnetic phase transition. The influence of the powder synthesis method on the structural, morphological, magnetic and magnetocaloric properties of the samples are investigated. The X-ray diffraction pattern shows reflections typical of the perovskite structure with orthorhombic symmetry. The experimental results reveal that both samples undergo a second-order phase transition. The maximum magnetic entropy changes, deduced from the $M-\mu_0H$ measurements, are 3.77 and 7.23 J/kg K under the magnetic field change of 5 T for $\text{Pr}_{0.8}\text{K}_{0.2}\text{MnO}_3$ synthesized by using solid-state reaction and sol–gel methods respectively. The field dependence of magnetic entropy change is analyzed showing the power law dependence, $\Delta S(T, \mu_0H) = a(T)(\mu_0H)^{n(T,H)}$ at the Curie temperature. Using the scaling laws of ΔS , the experimental ΔS collapse onto a universal curve for both ceramics. These results suggest that the physical properties of our samples are strongly depended on synthesis techniques. It is found that Pechini sol–gel method is more efficient and stable to obtain ceramic materials with good magnetic properties. Consequently, a substantial increase of the ferromagnetic to paramagnetic transition temperature and an enhancement of magnetocaloric properties are observed in the sol-gel made sample making it more suitable for magnetic refrigeration applications.

Keywords: Preparation methods, Magnetization, Magnetocaloric effect, Manganites

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Thematic Session: 1D Nanomaterials

Keywords: ZnO, Nanowires, Ga doping

Gallium doping of ZnO nanowires by chemical bath deposition

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Over the last decade, ZnO nanowires (NWs) have been used for a wide variety of optoelectronic devices, including UV self-powered photodetectors and solar cells. For all these applications, their electrical properties, such as their conductivity and mobility, should be controlled as much as possible. ZnO is intrinsically n-type owing to the high density of hydrogen [1, 2] and can intentionally be n-doped, for example, by Gallium. The doping of ZnO NWs has however been mainly performed by vapor deposition techniques. In the present work, ZnO NWs are doped with Gallium by using the low-cost, low-temperature, and easily implemented chemical bath deposition (CBD) technique. Gallium nitrate and ammonia are added in various concentrations to the standard precursors (i.e. zinc nitrate and HMTA [3]) in deionized water. It is shown by scanning and transmission electron microscopy (TEM) that this addition completely modifies the structural morphology of ZnO NWs. The formation mechanisms are thoroughly investigated and supported by thermodynamic simulations yielding speciation diagrams and solubility plots. The incorporation of Gallium dopants is further investigated by x-ray diffraction, energy dispersive x-ray spectrometry using scanning TEM, and temperature-dependent Raman spectroscopy. In particular, the occurrence of different additional modes in Raman spectra before and after annealing under oxygen atmosphere show the presence of the Gallium related defects and their incorporation mechanisms into ZnO NWs [4].

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The Nanoscience Meeting

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Centre des congrès Pierre Baudis

December, 8, 9 and 10



Thematic Session: (D & 2D Nanomaterials)

Keywords: (4-5 keywords are required)

On-surface synthesis of polymeric chains through C-S activation

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A variety of chemical reactions have been explored in on-surface synthesis to create original compounds by taking advantage of a solid surface acting as confinement template. Inspired by the Ullmann reaction, the C-C coupling between halogenated precursors has been first demonstrated and it is now the most widely used coupling mechanism. Besides, a few other mechanisms have also proven successful, most remarkably the direct C-H activation that is greatly facilitated by the role of the supporting metal surface. Nevertheless, it is of prime importance to investigate novel reaction mechanisms for on-surface synthesis for a better control and predictability of the reaction products and to position this newly developed field as an efficient and versatile chemical synthesis approach.

Transition metal-mediated activation of C-S bonds has been extensively investigated and sulfur-based organic synthesis is emerging as an alternative to halogen-based synthesis. Here we demonstrate that C-S bond activation represents similarly an efficient reaction pathway in the on-surface synthesis approach (See Figure 1).

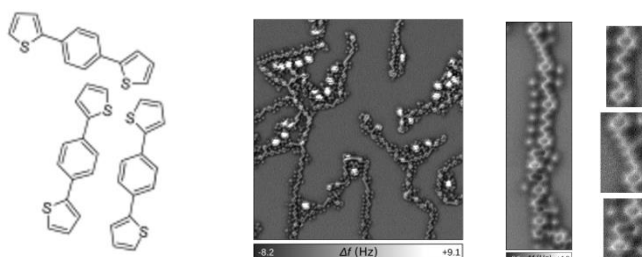


Figure 1. Polymer chains obtained upon polymerization of dithienylbenzene (DTB) on Cu(111) substrates.



P3 - NANO FOR IMAGING, DIAGNOSIS AND THERAPY

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Centre des congrès Pierre Baudis

December, 8, 9 and 10



Thematic Session: Nano for Imaging, diagnosis & therapy, Nanochemistry & Nanoparticles

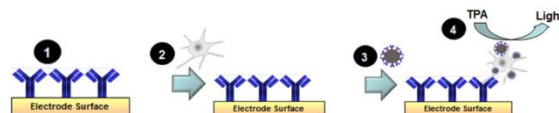
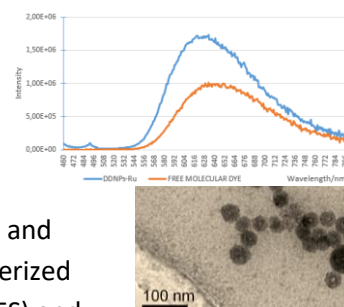
Keywords: pollutant sensing; electrochemiluminescence; ruthenium; dye doped silica nanoparticles

Detection of low amount of target pollutants in wastewater samples with dye doped, ECL-active silica nanoparticles

Federica Melinato¹, Errol Blart¹, Clémence Queffélec¹, Yann Pellegrin¹ and Robert J. Forster²

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The well-being of society leads to an increase of population and consequently to an increase of demand for tap water. In 2035, the estimated increase is 40% and new detection and removal systems for new pollutants (e.g. antibiotics) that are difficult to identify and remove are developed. Our goal consists in designing dye doped silica nanoparticles luminescent probes (**DDSNPs**), which could detect, the presence of pollutants before and after incineration treatment by electrochemiluminescence (**ECL**)¹ detection techniques. These luminescent sensors are made up of a silica shell which hosts luminescent Ruthenium (II) complexes. The strategy relies on the design of a series of dyes with pendant alkoxy silane function that will be hydrolyzed with a silica molecular precursor (e.g. tetraethoxysilane) yielding **DDSNPs**. Compared to the free-molecular dye in solution, suspensions of **DDSNPs** show enhanced stability and photophysical parameters. The formation of these nanoparticles will be performed by the two main synthesis pathways: normal microemulsion (path **A**) and reverse-microemulsion (path **B**). We performed both syntheses and fully characterized the obtained nano-objects from a morphological point of view (TEM, DLS, ICP-AES) and physical point of view (optical properties). The **DDSNPs** were post-functionalized with thiol pending groups to allow strong binding on a gold electrode². In suspension, the nanoparticles generate an intense ECL signal in presence of TPA as co-reactant. As illustrated, these **DDSNPs** are being used as labels within antibody sandwich assays for the highly sensitive detection of pathogenic bacteria, e.g. E. coli.



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December, 8, 9 and 10



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Acknowledgment: ANR for financial support through JPI waters.

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December, 8, 9 and 10



Thematic Session: Nano for Imaging, diagnosis and therapy

Keywords: Gaz-liquid interface, Fluidic force microscopy, Functionalization, Molecular interactions

Development of a method to access the interactions between gaz/liquid and biological interfaces

Irem Demir^{1,2}, Ines Lüchtfeld³, Claude Le Men¹, Pascal Guiraud¹, Etienne Dague², Tomaso Zambelli³ and Cécile Formosa-Dague¹

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The interactions between gaz/liquid interfaces (bubbles) and cells are involved in many bioprocesses. For example in bioreactors, breathing microorganisms interact with their growth medium but also with the gases present in the medium under the form of bubbles. While many studies are dedicated to the modelling of such processes, none of them have yet looked into the interactions between the cells and the bubbles. Thus questioning these interactions is highly original, and provides relevant data that can be used in many biotechnological applications. But accessing such interactions presents several technological challenges, the main one being to produce microsized bubbles, stable over time. In this presentation, we show recent developments in which we produce stable bubbles using FluidFM technology that combines AFM with microfluidic AFM probes¹. In this system, a micro-sized microfluidic channel is integrated in an AFM cantilever and connected to a pressure controller system, thus creating a continuous and closed fluidic conduit that can be filled with air, while the tool can be immersed in a liquid environment. An aperture at the end of the cantilever allows the air to be pushed out of the probe into the liquid, resulting in the creation of a bubble. Force feedback is then ensured by a standard AFM laser detection system that measures the deflection of the cantilever and thus, interactions can be probed directly with cells. Finally, the bubbles produced using this technique can be functionalized with surfactants, which allows to modulate the interactions between the bubble and cells.

References:

¹Meister *et al.*, NanoLetters 9, 6, 2501–2507, 2009

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December, 8, 9 and 10



Thematic Session: Nano for Imaging, diagnosis and therapy

Keywords: SERS, aptamer, bioreceptor, DNA, analyte.

Structural study of DNA interaction by Surface Enhanced Raman Scattering

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Surface Enhanced Raman Scattering (SERS) is a powerful tool to detect and study the structure of molecules. It is extensively used as sensor to observe biomolecules. The SERS substrate is then covered by a bioreceptor specific to the targeted analyte. One of the most used bioreceptor is aptamer, a single strand DNA, that exhibits a high affinity to the molecule to be detected through the formation of a specific secondary structure. In this communication, we addressed quantitative analysis of SERS spectra of one aptamer in interaction with its complementary DNA sequence. The complementary DNA was detected at very low concentration (down to 100 nM) and the analyte/aptamer interaction visualized. Moreover, by mapping the interaction on a 2D SERS substrate, we are able to observe spectral fluctuations that can be correlated to aptamer conformation modifications and to its stability as a function of its interaction with the complementary DNA. These results would open new detection and analytical strategy of SERS based bio-sensors using aptamers.

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Thematic Session: Nanos for Imaging, diagnosis and therapy

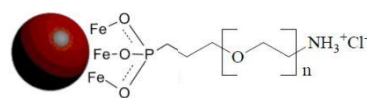
Keywords: magnetic nanoparticles, tumor targeting, magnetic hyperthermia

Bio-functionalized magnetic nanoparticles to study magnetic intra-lysosomal hyperthermia (MILH) on pancreatic endocrine cancer cells

Megi Bejko^{1,2}, Justine Journaux³, Véronique Gigoux³, Stéphane Mornet¹, and Olivier Sandre²

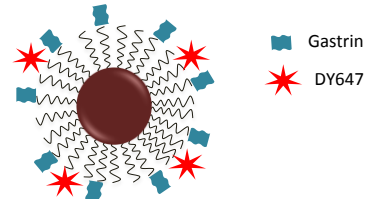
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Due to their unique properties, magnetic nanoparticles (MNPs) are very useful in nanomedicine for applications as vectors for targeted drug



NF@PEG-NH₂

Gastrin coating
DY647 for in vivo experiments



NF@PEG-Gastrin

delivery, MRI contrast agents and heating mediators in magnetic hyperthermia (MH). In 2011, MH was authorized to treat high grade brain tumors, when combined with radiotherapy (RT).¹ However, survival rate is still minute (average gain of 2 months lifetime) and neither RT nor MH can discriminate between normal and cancerous tissues, leading to undesirable side effects. Designing MNPs capable to specifically recognize cancerous cells is a strategy to achieve MF specifically at tumor sites by application of alternating magnetic field (AMF) while minimizing damage to healthy tissues. Moreover, magnetic intra-lysosomal hyperthermia (MIHL) is an approach where cancerous cells internalize specifically MNPs compared to healthy ones so that they can be killed by an AMF application, even without macroscopic temperature rise. In the context of a Canceropole GSO consortium project between our laboratories in Bordeaux and Toulouse, we study grafting of MNPs with a targeting peptide that recognizes CCK2 receptor overexpressed by pancreatic adenocarcinoma cancer cells. Once they accumulate inside lysosomes of tumor cells and an alternating magnetic field (AMF) is applied, MNPs provoke cell death.² This poster communication reports synthesis of iron oxide MNPs of high heating capacity, their surface modification with polymers (PEG chains), fluorescent probes (DY647) and gastrin, and their study *in vitro* (cellular uptake, cytotoxicity with/without AMF or chemotherapy) to prepare future *in vivo* assays.

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² P. Clerc, P. Jeanjean, N. Halalli, M. Gougeon, B. Pipy, J. Carrey, D. Fourmy, V. Gigoux, *J. Contr. Rel.* 2018 270, 120

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The Nanoscience Meeting

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December, 8, 9 and 10



Thematic Session: Nano for Imaging, diagnosis and therapy

Keywords: Gaz-liquid interface, Fluidic force microscopy, Functionalization, Molecular interactions

Development of a method to access the interactions between gaz/liquid and biological interfaces

Irem Demir^{1,2}, Ines Lüchtfeld³, Claude Le Men¹, Pascal Guiraud¹, Etienne Dague², Tomaso Zambelli³ and Cécile Formosa-Dague¹

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The interactions between gaz/liquid interfaces (bubbles) and cells are involved in many bioprocesses. For example in bioreactors, breathing microorganisms interact with their growth medium but also with the gases present in the medium under the form of bubbles. While many studies are dedicated to the modelling of such processes, none of them have yet looked into the interactions between the cells and the bubbles. Thus questioning these interactions is highly original, and provides relevant data that can be used in many biotechnological applications. But accessing such interactions presents several technological challenges, the main one being to produce microsized bubbles, stable over time. In this presentation, we show recent developments in which we produce stable bubbles using FluidFM technology that combines AFM with microfluidic AFM probes¹. In this system, a micro-sized microfluidic channel is integrated in an AFM cantilever and connected to a pressure controller system, thus creating a continuous and closed fluidic conduit that can be filled with air, while the tool can be immersed in a liquid environment. An aperture at the end of the cantilever allows the air to be pushed out of the probe into the liquid, resulting in the creation of a bubble. Force feedback is then ensured by a standard AFM laser detection system that measures the deflection of the cantilever and thus, interactions can be probed directly with cells. Finally, the bubbles produced using this technique can be functionalized with surfactants, which allows to modulate the interactions between the bubble and cells.

References:

¹Meister *et al.*, NanoLetters 9, 6, 2501–2507, 2009

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December, 8, 9 and 10



Thematic Session: Nano for imaging, diagnosis & theranostics

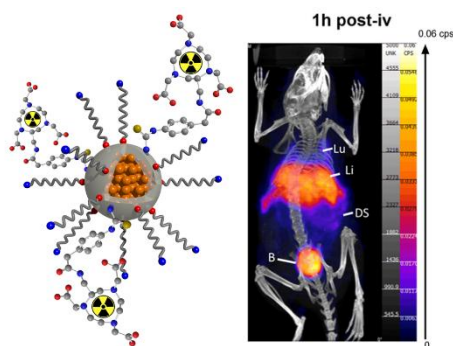
Keywords: Iron oxide, contrast agent, MRI, PET, cardiovascular disease

MRI-PET contrast agents based on Iron oxide Nanoparticles

G. Thomas¹, J. Boudon¹, L. Maurizi¹, M. Moreau², P. Walker³, A. Oudot⁴, I. Severin⁵, S. Poty², C. Goze², J.-M. Vrigneaud⁴, F. Demoisson¹, F. Denat², F. Brunotte⁴, N. Millot¹

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SuperParamagnetic Iron Oxide Nanoparticles (SPIONs) are widely used in biomedical applications (hyperthermia, drug delivery and T₂ contrast agents for MRI) [1]. These probes are thus a great tool for theranostics applications. For many years, our lab has developed nanoparticles with a narrow size distribution by means of a continuous hydrothermal process [2]. These particles can be coated *in situ* by organic molecules like catechols, in particular 3,4-dihydroxy-L-phenylalanine (L-DOPA) [5,6]. This type of ligand leads to an anti-oxidizing effect and an improvement of nanoparticle stability at physiological pH [3-4].



In this study, Fe₃O₄ nanoparticles used as contrast agent for MRI/PET double imaging have been developed. These multimodal agents are easily synthesized by a step-by-step aqueous protocol, with the successive grafting of MeO-PEG₂₀₀₀-NH₂ to confer both good colloidal stability and stealth properties in physiological conditions followed by the grafting of *p*-NCS-Bz-MANOTA to ensure the stable chelation of copper (⁶⁴Cu) for PET imaging [5].

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The elaborated imaging agents were fully characterized and are stable under physiological conditions. Yields of radiolabeling are good and indicate that the radioactive tracer is efficiently chelated by the grafted macrocycles. *In vitro*, *in vivo* and biodistribution results on the constituting elements of the final nanohybrid will be presented. Considering these preliminary results, the elaborated nanohybrids appear as promising contrast agents for MRI/PET double imaging with a view to cardiovascular diseases imaging.

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The Nanoscience Meeting

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December, 8, 9 and 10



Thematic Session: Nano for Imaging, diagnosis and therapy

Keywords: quantum dots, magnetic nanoparticles, bioconjugation, surface chemistry, live cell imaging

Zwitterionic nanoparticles for imaging and manipulating chromosomes in living cells

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In a cell nucleus DNA is organized in a complex 3D multiscale architecture. This architecture plays a role in DNA functions such as gene regulation, but this is not fully understood [1,2]. New techniques to study the dynamics of DNA in single living cells would be useful to better understand this architecture. In this project we propose to build fluorescent or magnetic nanoprobe that can bind to specific DNA sequences. We will use fluorescent quantum dots, highly bright and photostable nanoparticles to enable long term tracking of single DNA sequences. We will also use magnetic iron oxide nanoparticles to apply a mechanical force on a specific part of the genome. This will give a precise insight on how the genome is sensing a mechanical force and what is its effect on transcription. The first challenge lies in avoiding nonspecific interactions between the nanoprobe and biomolecules in the very crowded intranuclear environment. To achieve this, we have designed a specific diblock copolymer to coat the nanoparticles. The first block contains sulfobetaine zwitterions that are very efficient to eliminate nonspecific interactions [3]. The second block contains multiple anchoring groups to ensure long term anchoring stability. The absence of interactions with proteins with the selected polymer coating has been assessed in vitro and in cellulo. The second challenge is to conjugate specific CRISPR-Cas9 proteins that will enable targeting of selected DNA sequences. We have optimized the design of the polymer architecture to achieve controlled and efficient binding of targeting proteins to the surface of our nanoparticles.

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December, 8, 9 and 10



Thematic Session: Nanos for Imaging, diagnosis and therapy

Keywords: cancer, ultra-small superparamagnetic nanoparticles, targeted nanotherapy, rotating magnetic field, mechanical forces

Remote magneto-mechanical destruction of cancer-associated fibroblasts using targeted ultra-small superparamagnetic iron oxide nanoparticles and low frequency magnetic fields

Sara Lopez^{1,2}, Nicolas Halali¹, Yoann Lalatone³, Arnaud Hillion¹, Joana C Antunes³, Nizar Serhan^{1,2}, Pascal Clerc^{1,2}, Daniel Fourmy^{1,2}, Laurence Motte³, Julian Carrey¹, Gigoux Véronique^{1,2}.

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In the tumor microenvironment, cancer-associated fibroblasts (CAFs) promote growth and resistance acquisition of tumors as well as limit the penetration and diffusion of chemotherapeutic agents into the tumor by secreting collagen and increasing extracellular matrix density¹. In this context, the development of nanotherapy targeting tumor microenvironment represents a real opportunity to propose new therapeutic solutions. Alternatively to local heat release upon a high frequency alternating magnetic field exposure, magnetic nanoparticles generate torque or mechanical forces in response to a rotating low frequency magnetic field (RMF)². Such approach constitutes a technically easier approach compared to magnetic hyperthermia and with potentially less undesirable effects for patients.

Here, we developed ultra-small superparamagnetic iron oxide nanoparticles (USPION, 6-nm crystalline core) decorated with gastrin, which successfully targeted pancreatic adenocarcinoma CAFs expressing the CCK2 receptor and accumulated within their lysosomes. A screening in the magnetic field amplitude, frequency and type (rotating, alternating, static) demonstrated that cell death is maximized when the field rotates, and displayed a maximum as a function of the field amplitude. These features were expected theoretically and are supported by kinetic Monte-Carlo simulations, permitting to estimate that the force generated by USPIONs assembly is of the order of 3pN under optimal conditions. Using a 40mT/1Hz RMF, a 34% cell death ratio is reached. Finally, we showed that cell death occurs through a lysosomal pathway. This study establishes the proof-of-concept that targeted USPIONs can disrupt the tumor microenvironment through mechanical forces generated by a low frequency RMF, that opens new opportunities for cancer therapy.

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LSPR spectrum without aggregation. In contrast, in human serum Gal-PPMA-coated nanorods showed no binding response, while Gal-PHEA exhibited a dose-dependent blue-shift of the LSPR peak.

The behaviour of the assay showed a complex dependence on both the chemistry of the polymer coating and the composition of the test medium. Based on size distribution measurements of the glycoconjugated GNRs before and after lectin binding, the biomolecule corona was observed to play a key role both in the nanoparticle stabilization and in their interaction with SBA.

References (max. 5):

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Acknowledgment:

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December, 8, 9 and 10



Thematic Session: Nano for Imaging, diagnosis & therapy

Keywords: gold nanorods; glycopolymers; protein corona; biosensors.

The Nature of Polymeric Glyco-Ligands Controls the Signal Outputs for

Plasmonic Gold Nanorods Biosensors in Complex Media

Alessia Pancaro^{1,2}, Michal Szymonik¹, Panagiotis G. Georgiou³, Alexander N. Baker³, Marc Walker⁴, Peter Adriaensens⁵, Jelle Hendrix², Matthew. I. Gibson^{3,6} and Inge Nelissen¹

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

Gold nanorods (GNRs) are a promising platform for label-free plasmonic biosensing: their localized surface plasmon resonance (LSPR) signal is highly sensitive to refractive index changes in the local environment near the rod surface, such as those caused by binding of biomolecules.[1] Polymers are usually used to prevent aggregation, increase stability and control nanoparticle surface properties.[2] Carbohydrate-binding proteins, including lectins, which have been identified as potential biomarkers for human disease diagnosis,[3] are desirable targets for biosensing using glycopolymer-conjugated GNRs.

We studied the effect of the polymer ligand chemistry on the LSPR shift of glycoconjugated GNRs upon lectin binding in buffer and human serum.

Poly(N-(2-hydroxypropyl) methacrylamide) (PHPMA) and poly(N-hydroxyethyl acrylamide) (PHEA) homopolymers were synthesized by RAFT polymerization [4] and used as linkers to functionalize GNRs with 2-amino galactose (Gal).[5] Addition of soybean agglutinin (SBA) as a model lectin to Gal-PHEA-coated GNRs in buffer lead to aggregation, whereas Gal-PHPMA-coated GNRs exhibited a red-shift of the

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Thematic Session: Nano for Imaging, diagnosis and therapy

Keywords: Fluorescence, nanocarrier, PDT, porphyrin, singlet oxygen, two-photon imaging

Soft fluorescent organic nanoparticles as nanocarriers for PDT

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Abstract: Novel highly water-soluble soft fluorescent organic nanoparticles (FONPs) have been obtained using green synthesis protocols. These nanoparticles show remarkable solubility (>250 g/L), as well as bright blue fluorescence in aqueous environment that are fully retained in cell culture medium. These FONPs were shown to internalize into cancer cells while showing no cytotoxicity [1]. Furthermore, they offer versatile opportunities for surface functionalization as they present numerous acid (CO₂H) and amino (NH₂) groups. In particular, hydrophobic drugs such as paclitaxel can be covalently attached to the FONPs yielding conjugated FONPs (FONPs[PTX]) which retain both large water-solubility and fluorescence in aqueous environment and demonstrate cytotoxicity in glioblastoma cell lines [1].

These unique features were applied to anticancer photodynamic therapy. In this framework, we have covalently attached an efficient but hydrophobic photosensitizer, the prototypical tetraphenylporphyrin (TPP), yielding FONPs[TPP] which retain water solubility and exhibit the characteristic photophysical (intense absorption, red fluorescence) and photochemical properties of porphyrins (singlet oxygen generation). In particular, the absorption spectra demonstrate that the use of FONPs as nanocarriers prevents aggregation of TPP in water which would be deleterious to photosensitizing activity. In addition, FONPs[TPP] show bright red fluorescence in water allowing monitoring of their internalization by fluorescence microscopy [2]. Dramatic cell death (as assessed by bioluminescence imaging) was observed after short irradiation at 405 nm using LED as light source. These results open the route to novel biocompatible phototheranostics nanotools for cancer treatment.

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Functional Imaging with Higher-Dimensional Electrical Data Sets

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AFM-based nanoelectrical modes [1] have numerous applications in fields ranging from semiconductors to biology. The data produced have traditionally been in the form of a 2D map, generated in contact mode, with a single electrical data point per XY location. Electrical ramps or spectra would be generated at a few, carefully selected locations. This article discusses a new approach to nanoelectrical imaging that creates an electrical data cube and a correlated nanomechanical data cube while operating at normal imaging speeds. This approach avoids contact mode imaging, thus extending electrical measurements to soft and fragile samples and improving measurement consistency. Moreover, this is a general approach that is applicable to most nanoelectrical modes and applications.

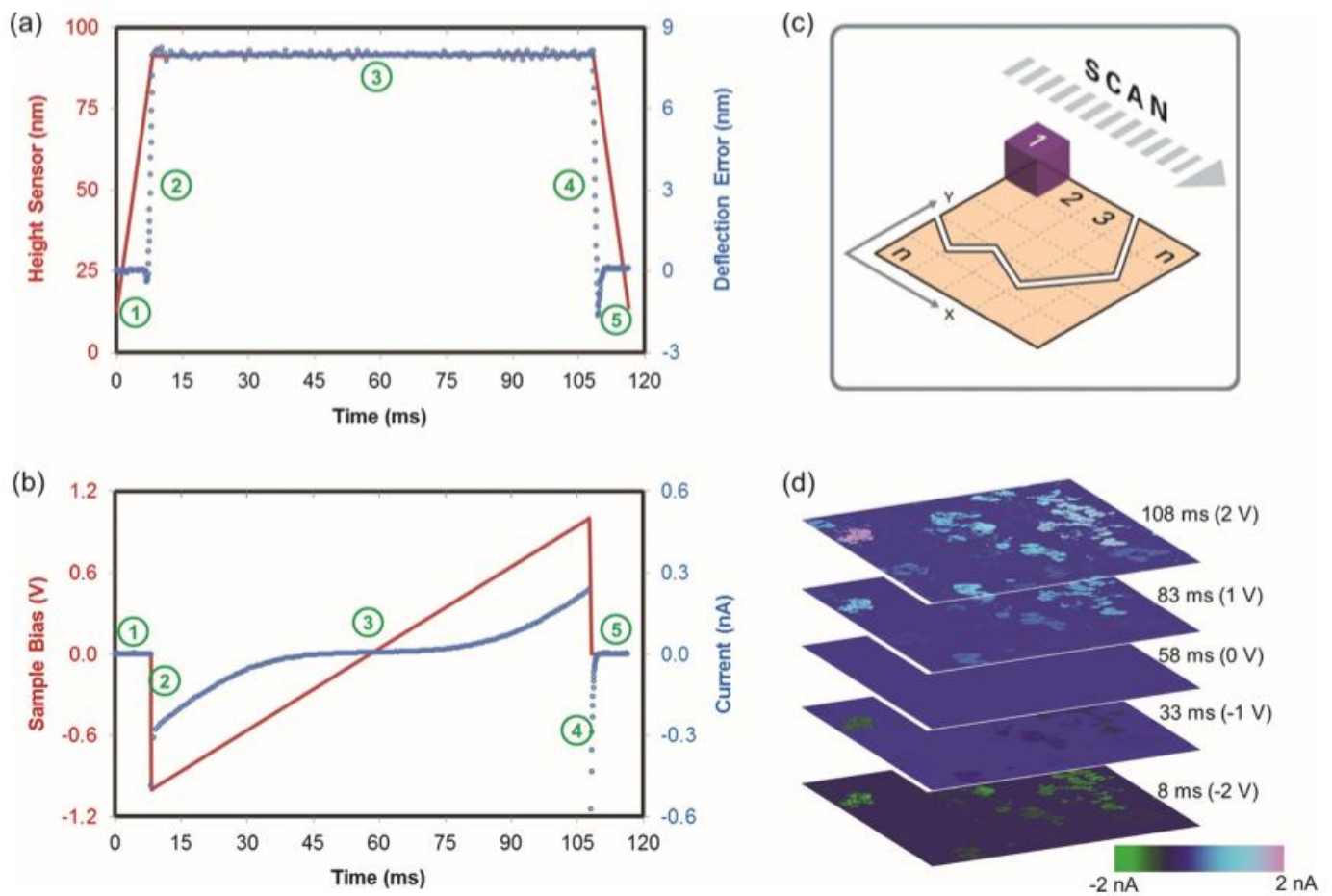


Figure 1 : Data cube (DCUBE) modes operating on fast force volume (FFV) approach: (a) height sensor (red) and deflection error (blue open circle) plots with segments showing extend (1–2), dwell (3), and retract (4–5) cycles; (b) pattern of sample bias (red) and corresponding tunneling AFM (TUNA) current (blue); (c) illustration of scan pattern during acquisition of DCUBE-mode data; and (d) five TUNA current slices from the DCUBE-TUNA results.

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P4 - NANOCHEMISTRY & NANOPARTICLES

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Drug delivery systems, Rifampicin, nanoparticles, encapsulation, biodegradable polymer

Nanoemulsions for biomedical applications: drug-loaded size-controlled biodegradable polymeric nanoparticles

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Abstract:

Producing smaller and smaller nanoparticles becomes a trend which main motivation is to diversify their application fields, such as sensorics or drug delivery systems. For the latter, biodegradable polymeric nanoparticles are considered as promising materials¹ since these; small particles favor drug targeting and may prevent the recognition by the immune system.

In this context, poly(lactic-co-glycolic acid) PLGA nanoparticles were obtained by emulsification- evaporation method with three different devices (rotor-stator mixing, sonication and elongational-flow micromixing). Transmission electron microscopy (TEM) images and dynamic light scattering (DLS) measurements were realized in order to investigate the nanoparticles' size and their size distribution through the evaluation of the polydispersity index (PDI). This study lead to the determination of optimal mixing parameters (number of cycles, duration, rotation speed) for the three devices and the formation of PLGA nanoparticles of various controlled diameters (ranging from 60 to 200 nm) to compare with previous studies.²⁻⁴ Our team also successfully achieved the one-step encapsulation of up to 42% of a hydrophobic drug (Rifampicin) inside the PLGA nanoparticles by the elongational-flow micromixing. For example, within 8 days 234 µg *in-vitro* drug release was investigated at 5% drug load (395 µg).

As a conclusion, we highlighted very encouraging results to further develop biomedical-related systems: the possibility to obtain monomodal biodegradable, biocompatible polymer nanoparticles in which (bio)molecules can be encapsulated and released from them.

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Thematic Session: Nanochemistry and Nanoparticles

Keywords: nanoparticle synthesis, solid-state metathesis, carbides, energy-efficient

Early Transition Metal Nanocarbides and Nanohydrides by Solid-State Metathesis initiated at Room Temperature

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Metal carbides are materials of high interest due to their catalytic activity (RWGS, HER, hydrogenation). [1] We recently developed a thermally self-sustained reaction to form nanoparticles (< 50 nm diameter) dispersed on a carbon support *via* a solid-state metathesis between a metal chloride (MCl_x) and metallic potassium dispersed in carbon (KC_4/KC_8) (*cf.* Figure 1, left). [2] The potassium reduces the metal center to form KCl and carbide or metallic nanoparticles, the latter being eventually converted into hydrides. Beyond the advantages of this innovative process in terms of green chemistry (no solvent, no extensive heating and innocuous wastes), the reaction is versatile and was successfully applied to numerous early transition metals (Ti, V, Zr, Nb, Mo, Hf, Ta, W).

In the present work, we studied the impact of different process parameters (atmosphere, carbon support...) on the metal speciation, by Powder X-ray Diffraction (PXRD), and on the morphology of the nanoparticles, by Transmission Electron Microscopy (TEM) (*cf.* Figure 1). We could then propose a general mechanism for the different steps of the reaction.

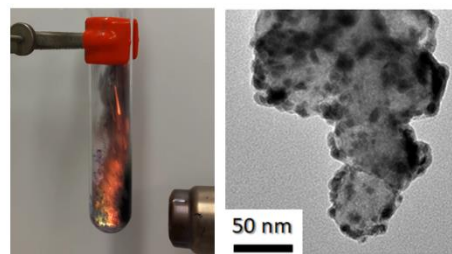
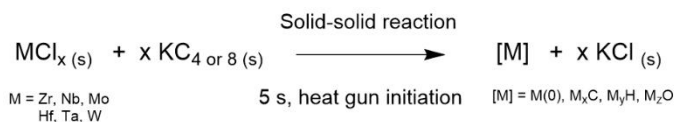


Figure 1: Solid-state synthesis of W_2C nanoparticles on carbon support (reaction snapshot and TEM picture)

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Thematic Session: Nanochemistry & nanoparticles

Keywords: silver, cubes, supercrystal, sintering, electronics

Synthesis, self-assembly and sintering of silver nanocrystals for electronics

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The interest of silver nanostructures has surged in recent years as they are becoming promising materials in a growing number of applications. In particular, they have received intense attention for their use as lead-free die attach materials, photoactive devices engineering or more broadly electronic packaging. One of the challenges is the elaboration of conductive and printable patterns by Low-Temperature and Pressureless Sintering Techniques (LTPST) to achieve electric circuits on dielectric substrates such as ceramic, plastic, polymeric, substrates. Here, we present a facile method for synthesizing conductive patterns at low temperature based on the formation of self-assembled Ag nanocubes on Active Metal Brazing substrates. The elaboration of 3-D arrays with nanogap of 2-3 nm between the cubic building units allows to get dense and compact packed nanoparticle solids which sinter at lower temperature than commercial silver paste. The impact of the capping agent and the size of the building units on the sintering properties were investigated and will be discussed.

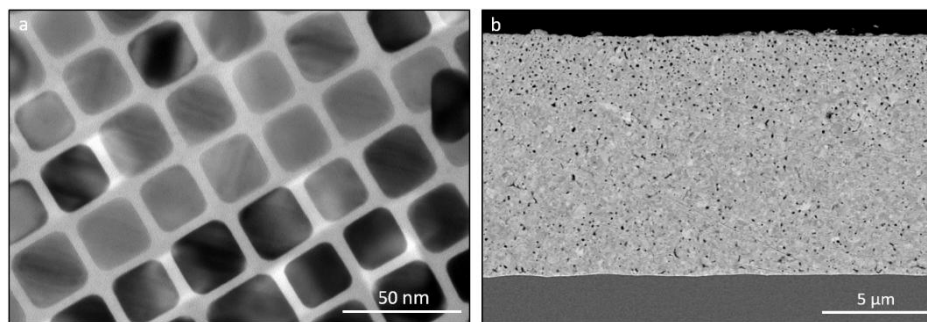


Figure. (a) Silver Nanocubes produced by wet chemistry (b) Sintered material produced from Ag Nanocubes.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Nucleation mechanisms, in-situ studies, X-Ray diffusion, non-classical nucleation

Liquid-liquid phase separation during the precipitation of cerium oxalate

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Nucleation is one of the most common schemes of crystallization. It is usually explained by thermal fluctuations of the reaction media leading to the formation of clusters, which tend to dissolve instead of growing unless they reach a critical nucleation size¹. However, it has been evidenced that this classical depiction is far from correct: it assumes in particular that the clusters have directly the symmetry and thermodynamic properties of the bulk crystal, whereas crystallization is often "non-classical" and occurs through non-crystalline intermediates^{2,3}.

Here we show using in situ SAXS and cryo-TEM that cerium oxalate follows two possible non-classical nucleation mechanisms: at low concentrations, nucleation in the presence of amorphous nanoparticles, and at higher concentration, nucleation involving both the amorphous particles and droplets of a reactant-rich liquid phase.

These results call for a revision of the modeling of industrial precipitation processes based on oxalic precipitation, such as the recovery of rare earths and actinides, which are currently based on the classical crystallization scheme and ignore both nanophases⁴.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Nanoparticles, Reproducibility, Polymer, Impurity

Polyvinylpyrrolidone (PVP) impurities drastically impact the outcome of nanoparticle syntheses

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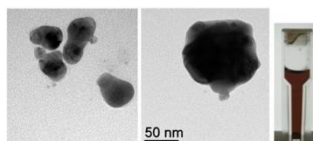
Abstract:

Polymer additives such as Polyvinylpyrrolidone (PVP) are ubiquitously used in wet chemical reduction methods to tune nanoparticle sizes and shapes. However, all polymers retain some traces of their synthetic history through their end-groups and impurities. These impurities may thus impact redox and interfacial processes occurring during the formation of nanocolloids.

We report a systematic comparison of four representative silver nanoparticle syntheses in the presence of either commercial PVP or its purified version, obtained through dialysis or filtration. We characterized the resulting nanoparticle dispersions through UV-visible spectroscopy, electron microscopy, X-ray scattering and Raman spectroscopy.

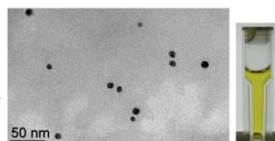
For all syntheses and methods, the simple removal of PVP molecular impurities drastically modifies nanoparticle size, shape and formation kinetic. Impurities from additives thus play a pivotal role in nanoparticle syntheses and must be systematically evaluated for relevant mechanistic investigations and robust process engineering. As an illustration, we show that oxidizing impurities underlie the formation of silver nanodisks in the presence of PVP.

Ag nanoparticles synthesized with **commercial** PVP



removing impurities

Ag nanoparticles synthesized with **purified** PVP



Reference:

N. El Amri, K. Roger, Polyvinylpyrrolidone (PVP) impurities drastically impact the outcome of nanoparticle syntheses, *Journal of Colloid and Interface Science*, **2020**

<https://doi.org/10.1016/j.jcis.2020.04.113>.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Nanoparticles, oxides, Magneli phases, molten salts, water remediation

Molten salts synthesis of Ti_4O_7 and compositional core-shell $V_{3.7}Ti_{0.3}O_7$ Magneli phases nanoparticles: a novel approach

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Ti_4O_7 , a member of the oxides family called Magneli phases, Ti_nO_{2-1} ($4 \leq n \leq 9$), has been historically studied as electrode for harsh conditions use and as thermoelectric material owing to its metallic behavior related to the coexistence of Ti^{4+} and Ti^{3+} . A renewal of interest for this material is occurring thanks to its potential as cathode materials for Li-sulfur batteries and electrolytic wastewater remediation, among others.^{1,2} Because these applications require a high surface-to-volume ratio, the design of synthetic pathways which allow achieving nanostructured Magneli phases becomes necessary.

Most synthesis attempts have been devoted to reduce TiO_2 nanoparticles employing different reductants, such as carbon species³ or dihydrogen⁴. These reductions are carried out at high temperature favoring crystal growth. We have capitalized on previous works reporting the use of hydride reducing agents to yield low valence oxides such as Ti_2O_3 ,⁵ in order to open a new pathway for obtaining Magneli phases at lower temperatures than in conventional synthesis. We will present a new synthetic route based on the liquid-phase reduction of TiO_2 by hydrides in molten salts towards Ti_4O_7 nanoparticles. We will discuss in depth the impact of the synthesis conditions on the resulting nanomaterials. We will show how versatile is this pathway by reporting isostructural materials, especially compositional core-shell nanoparticles $V_{3.7}Ti_{0.3}O_7$, never reported before. We will then discuss the interest of these new nanomaterials for electrochemical oxidation of wastes in water.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Boron, nanoparticles, ceramics, hardness, high pressure

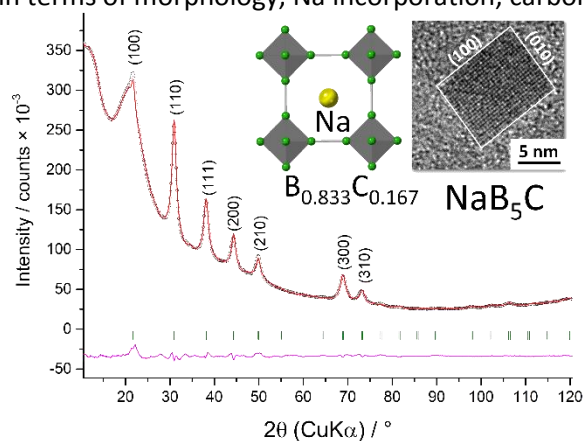
Synthesis inspired by geology towards new boron-based nanomaterials

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Exploratory chemistry in the solid state is a fascinating field that despite its uncertainty, can lead to astonishing discoveries. Development of novel synthetic strategies has been particularly relevant in the exploration of materials science at the nanoscale, impacting plasmonic, catalytic and hardness properties, many times unimaginable beforehand.[1] Boron-based solids are a particularly interesting and challenging system to bring to the nanoscale: its characteristic extended networks of covalent bonds require elevated energies in order to organize.[2] We herein discuss the use of synthetic paths inspired by geological processes, specifically the use of molten salts as reaction media and of elevated pressures in the GPa range, which provide relatively mild conditions to yield so-far unknown nanocrystalline solids.

The decomposition of NaBH_4 in molten sodium iodide and in the presence of polymeric sources of carbon atoms yields phase pure, *c.a.* 5 nm large, NaB_5C nanoparticles as depicted in the Figure. This phase exhibits an intriguing structural evolution towards superhard boron carbides upon heat treatment at temperatures above 1200 °C, where nanostructuring is preserved. This transformation is studied at ambient and high pressures, the latter through the use of Paris-Edinburgh and multi-anvil presses. The mechanical properties are studied by the Vickers method. Structure-property relationships are discussed in terms of morphology, Na incorporation, carbon content and synthetic conditions.



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Thematic Session: Nanochemistry & Nanoparticles

Keywords: porphyrin, platinum nanoparticle, Coulomb blockade, photoluminescence, self-assembly.

New platinum-porphyrin self-assembled nanostructures

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Colloidal nanoparticles are intensely studied in current nanoscience research due to their simple synthesis that allows to have ultra-small nanoparticles (US NPs) and their potential applications ranging from microelectronics to catalysis. Our project is focused on the ligand control of ultra-small metal nanoparticles self-assemblies (SA). Due to approximately the same size of nanoparticles and ligands they can alter properties of nanoparticles and help create new types of assemblies depending on the nature of the ligand.

In our study, platinum nanoparticle-porphyrin assemblies were formed by binding functionalized porphyrins to « naked » (stabilized only by CO and solvent THF) US Pt-NPs. SA with pyridine-monofunctionalized porphyrins form rod-shaped superstructures (Fig. 1, up) whereas pyridine-bifunctionalized porphyrins form sphere-shaped assemblies (Fig.1, bottom). Synthesized SA were tested in charge transport and photoluminescence (PL) experiments. We have found that SA with 0.05 eq of porphyrins show Coulomb blockade at room temperature. PL measurements showed decrease of porphyrins' fluorescence intensity with increased amount of Pt-NPs due to static quenching of porphyrins luminescence. Remarkably, the values of PL intensity decrease depend on the type of bonding between NPs and ligands. Using these results, we have described a simple method to evaluate the binding strength of porphyrins to Pt-NPs.

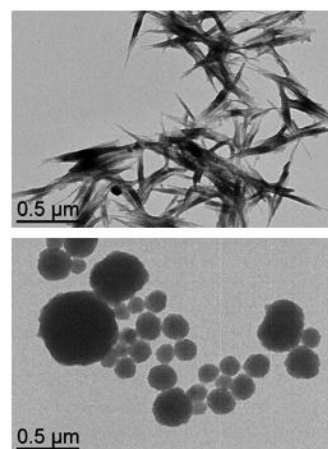


Fig.1

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: hydrodeoxygenation, biomass valorization, magnetic nanoparticles, magnetic catalysis

Hydrodeoxygenation of biomass-derived molecules using magnetic induction

Irene Mustieles Marin¹, Déborah de Masi¹, Juan M. Asensio¹, Lise-Marie Lacroix¹, Piet W. N. M. van Leeuwen¹ and Bruno Chaudret^{1*}

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Valorization of biomass products is gaining increasing attention due to need to find new fuel resources other than fossil. For example, 2,5-dimethylfuran, deriving from lignocellulose, appears as a promising candidate to be used as biofuel.¹ The separation of lignin from the cellulosic part leads to the generation of platform molecules, which after a hydrodeoxygenation reaction, can be converted in valuable chemicals. This transformation is generally catalyzed by noble metals at high H₂ pressures and temperatures. Magnetic induction has demonstrated to be very effective in solid-gas catalysis² but also in solution,³ rendering the temperature and pressure conditions milder compared to those used with conventional heating.

In this work, we present the catalytic conversion of biomass-derived products by application of magnetic heating and using a non-noble metal catalyst, FeNi₃ nanoparticles (NPs).⁴ FeNi₃ NPs allowed us to activate the C-O bond of different biomass-derived molecules. Hydrodeoxygenation of furfural derivatives and the cleavage of lignin model molecules, such as benzyl phenyl ether, were successfully achieved employing very low pressures of H₂ (3 bar).

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Thematic Session: Nanochemistry & nanoparticles

Keywords: bimetallic nanoparticles, silica, hydrogenation, catalysis.

Synthesis of supported FeNi nanocatalysts by an organometallic route.

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This project falls within an environmental approach where the purpose is to replace the noble metals by tunable and low-cost substitutes in supported nanocatalysts used by the food-processing industry for the hydrogenation of sugars into polyols [1]. We focus on the development of scalable synthesis routes towards bimetallic Fe-based supported nanoparticles (NPs)[2], and more precisely FeNi NPs with a special interest in the distribution of each element inside the nanoparticles, and its possible influence on their catalytic properties. For this purpose, an organometallic approach is chosen, based on the experience of our research group. It involves a controlled decomposition of organometallic and/or metal-organic complexes and a stabilization of the nanoparticles by organic ligands [3]. From the hydrogenation of $[\text{Ni}(\text{COD})_2]$ and $\{\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2\}_2$ complexes, at 150°C under 3 bar of H_2 , nanoparticles of three compositions were synthesized (Fe_9Ni_1 , Fe_1Ni_1 , Fe_1Ni_2) and fully characterized (ICP-AES analysis, TEM, EDX, WAXS, and Squid measurements). For some systems, a core-shell organization was identified with preferential location of Ni in the core and Fe at the surface (Figure 1). These NPs were deposited on silica beads as a support for their evaluation in hydrogenation catalysis.

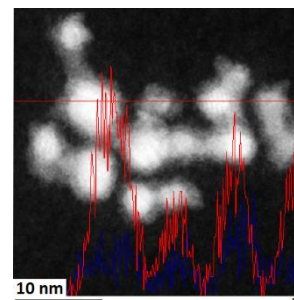


Figure 1 : NPs Fe_xNi_z analysed by ARM in STEM and EDX mode (red line ; Fe = blue, Ni = red).

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Thematic Session: Nanochemistry&nanoparticles

Keywords: Hydrogen, Photocatalysis, Ruthenium, Hybrids

Ru nanoparticles for photocatalytic hydrogen evolution

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The replacement of fossil fuels by renewable energy sources is one of the most urgent societal issues. An attractive solution is the production of hydrogen from water splitting (WS), using sunlight as driving force.¹ In this context, Ru nanocatalysts have demonstrated to be often as efficient as Pt materials for the hydrogen evolution (HE) half reaction.^{2,3} The present work is focused on the visible-light induced generation of hydrogen at neutral pH, using Ru nanoparticles⁴ onto titanium dioxide (RuNPs/TiO₂), [Ru(bpy)₂(4,4'-(PO₃H₂)₂(bpy))]Cl₂ and triethanolamine, as catalyst, photosensitizer and sacrificial electron donor, respectively. The nanocatalysts were prepared by the organometallic approach followed by impregnation onto TiO₂ (Figure 1). As observed through laser flash photolysis, the covalent bond between the photosensitizer and the TiO₂ enables the electronic communication between nanocatalyst and photoabsorber through the semiconductor, improving the photocatalytic performance of the system. The nanomaterial shows long-term stability under catalytic conditions.⁵

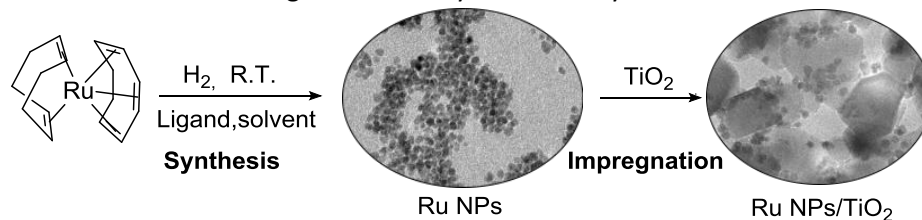


Figure 1. Synthesis of Ru nanoparticles onto TiO₂

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The Nanoscience Meeting

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December, 8, 9 and 10



Thematic Session: Nanochemistry & Nanoparticles

Keywords: Nanobelts, Dehydrogenation, Carbon chain, PAH, Space, Carbynes, Fullerenes

Chain formation by dehydrogenation of curved polyaromatic hydrocarbons

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Abstract

Carbon nanobelts, ultra-short single walled carbon nanotubes or closed graphene nanoribbon with hydrogenated armchair edges have first been synthesised in 2017 [1]. These unique structures have been proposed as building blocks for the bottom-up synthesis of carbon nanotubes with a highly oriented chirality. In our case they serve as an excellent uniform example of a curved polycyclic aromatic hydrocarbon, to explore dehydrogenation processes likely to occur in the interstellar medium in space.

We present the dehydrogenation process of [12]-carbon nanobelt (CNB, $C_{48}H_{24}$) when ionised and then damaged through gas-phase collision, before characterisation via mass spectrometry. We detect several specific mass signals and their molecular structures were theoretically explored by DFT calculations.

We performed sequential optimisations under +1 charge state for all possible structural isomers of each $C_{48}H_{24-n}$ ($n=1\dots 8$) to “map” the dehydrogenation process. There are several interesting dehydrogenation routes; (a) closure towards fullerene-like cages (b) unravelling into distinct carbyne-like carbon chains, and (c) opening into carbyne-like chains with pentagon ends. Both fullerene and carbyne-like signals are seen in interstellar medium spectra. We will discuss the most probably dehydrogenation process from the experimental mass spectra and the theoretical optimisation results [2].

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Acknowledgment:

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December, 8, 9 and 10



Thematic Session: (Nanochemistry & Nanoparticles)

Keywords: (Spark discharge, plasma in-water, nanoparticle, core-shell)

Study of synthesis condition for pure and compound metal nanoparticle

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The use of electrical discharges in liquid constitutes an efficient way to produce nanoparticles, by performing a controlled erosion of the electrodes [1]. This paper focuses on short pulsed discharges (duration < 500 ns, frequency of 100 Hz) in liquids. The goal is to study the process performances and getting information on the nanoparticles synthesis as a function of operational parameters. The power supply can set the discharge characteristics (voltage, duration) and the setup allows easy modification of electrode configuration and composition. Tip to tip or plane-tip operation are considered with different polarities, and the influence of the electrode gap is studied. A wide variety of metal can be used for electrodes, such as iron, copper, aluminum or molybdenum. When different metals are used for the two electrodes (such as Ni and Co) it is then possible to create core-shell structure or nanoalloy.

Depending on the experimental conditions, a cavitation bubble is formed in the liquid after the discharge. The evolution of its diameter is used to determine the pressure inside the bubble. In addition, the study of the erosion pattern on the electrodes surface can give information on the ablation process and the efficiency of the process to convert solid electrodes into nanoparticles.

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December, 8, 9 and 10



Thematic Session: Nanochemistry & Nanoparticles

Keywords: polyelectrolyte nanoparticles, emulsification-evaporation, elongational-flow, biocompatible polymer

One-step Production of Polyelectrolyte Nanoparticles

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Abstract:

Producing smaller and smaller neutral nanoparticles becomes a trend which main motivation is to diversify their application fields, such as drug delivery, biosensing or environmental research. However, charged polymeric nanoparticles did not yet find such success mainly due to the multi-step and time-consuming conventional production route.^[1]

We propose here, for the first time, to extend the emulsification-evaporation method to the one-step production of negatively charged polymeric nanoparticles. In this purpose, we studied the possible formation of polyelectrolyte nanoparticles (PNPs) of poly(styrene sulfonate) by various processes: rotor-stator mixing (forming nanodroplets by shearing forces), sonication (promoting nanodroplets' implosion) and elongational-flow micromixing (μ RMX). We were able to control the particles' sizes, ranging from 30 to 300 nm, and they were smaller than the one obtained in other studies.^[2,3] We found that only μ RMX allowed the production of highly monodispersed PNPs. Finally, we observed and explained the causes of an unusual behavior: the sudden increase of PNPs' size after a given emulsification time when using the elongational-flow reactor and mixer.

As a conclusion, we highlighted very interesting results concerning the controlled one-step production of monodispersed PNPs which size can be tuned only by varying process parameters. The use of PNPs in therapeutic delivery, biotechnology or diagnostic imaging would allow to combine the advantages of inorganic charged particles and the biocompatibility of polymers.

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December, 8, 9 and 10



Thematic Session: Nanochemistry and Nanoparticles

Keywords: Nanomaterials, Bimetallic nanowires, Optoelectronics, Transparent electrodes

Metal welding at room conditions of Cu@Ni bimetallic nanowire networks

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Abstract:

Transparent electrodes (TE) are essential components in a large range of modern-day devices such as solar cells, touch screens, Light Emitting Diodes (LED), transparent heaters¹ etc. Currently, the most prominent material used for TE purposes is indium doped tin oxide (ITO). Although the latter exhibits very good physical properties in terms of electrical conductivity and optical transparency, indium is scarce and hence expensive, and is a brittle material. Metallic nanowires (MNWs) represent a promising emerging material for TE due to their desirable optical and electrical properties, flexibility, as well as a more accessible price range.^[2, 3] In this communication, we will explore a bimetallic NW system comprised of a Cu core and a Ni shell, as pure Cu NWs lack chemical and thermal stability due to rapid oxidation⁴. We report a novel synthesis, as well as a novel way of optimizing conductivity in a Cu@Ni NW network by enhancing interconnectivity – a hydrazine vapor based reducing treatment at room conditions. In addition, we have investigated the extent of protection that the Ni shell provides in regard to chemical and thermal stability. No significant changes in the electrical conductivity have been measured in the course of six months following the hydrazine vapor based reducing treatment, deeming the created TEs stable long-term. Moreover, we demonstrate that the Cu@Ni NW have good stability when submitted to thermal stress.

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POSTPONED



**NEW
DATES**

**November
23, 24, 25
2021**

Thematic Session: Nanochemistry and Nanoparticles

Keywords: Silicon Nanoparticles, Precursor Decomposition, Metamaterials

Synthesis of Silicon Nanoparticles from an Azadipyromethene Coordination Complex

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Abstract:

Silicon particles are used in dielectric metamaterials because of their high refractive index and low absorption coefficient for visible light¹. While crystalline silicon has exceptional optical properties in comparison to other materials, it is very difficult to synthesize stable silicon nanomaterials². This communication presents a more flexible bottom-up synthesis method to produce silicon nanoparticles. The route involves a multi-step synthesis of a silicon(IV) azadipyromethene (Azadpm) coordination complex³. Following the synthesis of the coordination complex, the silicon precursor is thermally decomposed under reducing conditions to afford silicon nanoparticles. Three methods of thermal decomposition explore the effect of gases and heating conditions on the resulting silicon nanoparticles. The three methods involve: microwave heating under argon, heating in an oil bath under argon, and heating in an oil bath under hydrogen. Under each condition, the precursor material decomposes and affords silicon nanoparticles; however, each method results in nanoparticles of different sizes and morphologies.

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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: (Silicon-based nanoparticles, supercritical fluids, coordination complex, electron microscopy)

Synthesis of silicon-based nanoparticles by thermal decomposition of a silicon complex in supercritical n-hexane

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Abstract

We propose a synthesis in supercritical n-hexane, in a temperature range between 350 and 450°C and at a pressure of 250 bar using the complex (N,N'-diisopropylbutylamidinate) dichlorosilane ($[(iPr-N)_2C(C_4H_9)]_2SiCl_2$) to form silicon and silicon nitride particles. Previously, our group has already obtained silicon-based particles with a silicon core and an oxynitride (SiO_xN_y) shell using trisilane and the bisamidinate silicon precursor in supercritical n-hexane at 460°C and 300 bar [1]. Here we evaluate the thermal decomposition of the silicon bisamidinate complex alone, a precursor that is less dangerous and easier to obtain than trisilane. Irregular and cubic nanoparticles ~20 nm in diameter resulted from this synthetic approach. The distribution in shape and size changed according to the reaction temperature. The cubic shaped particles were composed of silicon and made up around 95% of the sample. The other nanoparticles indexed to $\gamma-Si_3N_4$ nanocrystals, which have never before been formed under such mild conditions. The dispersion of nanoparticles in hexane shows bright blue luminescence under irradiation with a 365 nm UV lamp. This behavior matches with the shoulder peak observed at 386 nm observed in the UV-VIS absorption spectrum. This electronic transference corresponds to direct transitions at the Γ or X point [2]. We hypothesize that the hexacoordinate silicon complex employed as a precursor, having the geometry of a distorted octahedron, favors the growth of the cubic Si_3N_4 phase, containing hexacoordinate silicon atoms. In future work, we will be conducting energy mapping of the $\gamma-Si_3N_4$ nanocrystals.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: nanorods, cobalt, core@shell, gold

Coating cobalt nanorods with gold containing shells

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For applications concerning permanent-magnets, cobalt nanorods (Co NRs) are ideal candidates thanks to their high saturation magnetization and high magnetic anisotropy.¹ However, the air- and water-sensitivity of Co renders them inappropriate for use in aqueous environment, such as biomedical applications. Coating Co NRs with a noble metal shell can protect them against oxidation.² It can also attribute magneto-plasmonic properties,³ allowing their use as contrast agents for magnetic imaging. The ideal noble metal for such coating is gold, however Co and Au are not compatible. Obtaining a continuous and thick layer of Au, to optimize their magneto-plasmonic properties, is a real challenge. Co NRs synthesized by the organometallic or the polyol method have different surface properties, that could be exploited towards the development of a continuous Au shell. For Co NRs prepared by the organometallic method, we focalized on two different compositions: Co@SnNiAu and Co@SnCuAu, while for the polyol-nanorods the first objective was to achieve a conformal oxide interlayer (Fe_xO_y and SiO_2), and subsequently grow a Au shell. Atomic resolution electron microscopy characterization of the organometallic-nanorods, highlights how the introduction of Sn and Ni or Cu layer is crucial for improving the homogeneity and the thickness of the gold shell, overcoming the Co-Au incompatibility. For the polyol-nanorods electron microscopy showed the formation of a thick layer of oxide shell for Co@CoO@ Fe_xO_y and Co@CoO@ SiO_2 , which prevent the full oxidation of the nanorods.

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The Nanoscience Meeting

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December, 8, 9 and 10



Thematic Session: (Nanochemistry & Nanoparticles)

Keywords: (CO₂, hydrogenation, catalysts, nanoparticles, TiO₂)

TiO₂ supported catalysts for CO₂ hydrogenation to C₂₊ products

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CO₂ conversion to valuable products is a necessary step toward the sustainable development of our societies. While the hydrogenation to C₁ products (CO, CH₄, CH₃OH, etc.) is relatively well mastered, the production of C₂₊ molecules is still challenging [1]. The thermocatalytic CO₂ hydrogenation to liquid hydrocarbons can be achieved *via* CO₂ modified FTS mechanism [1]. The latter requires two reactions in series: the reverse water gas shift reaction (RWGS) for the initial hydrogenation of CO₂ to CO; followed by the Fischer Tropsch synthesis (FTS) for the conversion of CO to C₂₊. Thus, the main objective of this work is to design a convenient catalyst system that allows performing both steps of CO₂ hydrogenation into C₂₊ in a fixed-bed reactor.

The targeted catalyst system is based on Pd and Co nanoparticles supported on commercial and modified TiO₂ supports. The two different supports allow uniformly control Pd particles size between 1.1 and 2.5 nm. Larger Pd nanoparticles with higher electron density exhibit higher activity during RWGS reaction due to their strong H₂ dissociation ability [2]. Moreover, the catalysts prepared on an appropriately modified support show higher activity than those prepared on the commercial support during CO₂-FTS catalytic tests, at temperatures as low as 220 and 250 °C. Different operating conditions allow modifying the product selectivity toward CO, CH₄, C₂-C₄ and C₅₊. Under selected conditions, the selectivity to C₅₊ can be maintained above 50%.

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**NEW
DATES**

**November
23, 24, 25
2021**

Thematic Session: Nanochemistry & Nanoparticles

Keywords: Viscosity, Surface Tension, Convective Assembly, Dip-Coating, Colloidal Monolayer

Solvent Viscosity and Surface Tension in the Control of Two Dimensional Convectively Assembled Nanoparticle Films

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Dip-coating in the evaporative regime offers a straightforward method for the self-assembly of nanomaterials into two-dimensional close-packed monolayers. However, certain conditions, such as small nanoparticles at low concentration require a set of dip-coating parameters that result in undesirable effects such as meniscus pinning. These effects typically cause the formation of inhomogeneous films, which feature the regular striped pattern of 'stick-slip' or multilayer regions. It remains an open problem to effectively address these issues and expand the range of suitable nanoparticles which can be reliably self-assembled by convective assembly techniques.

We present recent experimental results showing that solvent viscosity is an effective tool to control surface coverage. Silica spheres were suspended in a series of alcoholic solvents having similar surface tension, boiling point and density, but different viscosities. By isolating the impact of viscosity on film formation, stick-slip behavior was most pronounced at low viscosity and low withdrawal speeds. Increased viscosity resulted in lower distances between stick-slip bands and more homogeneous deposition. Surface tension was modified by adding glycerol to the solution. Surface tension plays a role in both particle pinning and in convective currents within the meniscus. Particularly, if there is a temperature gradient across the drying zone, the surface tension will vary, leading to the Benard-Marangoni effect. We illustrate this phenomenon using both spherical and anisotropic helical particles.

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December, 8, 9 and 10



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Acknowledgment:

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Rhodium, carbon nitride, SACs, hydroformylation of olefins

Rh single atoms highly dispersed on g-C₃N₄ as an alternative to the use of conventional catalysts for hydroformylation reaction

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Hydroformylation (HF) reaction is one of the main industrial processes for the production of aldehydes from olefins and syngas (CO and H₂)¹. Besides the difficulty of the recovery of the catalysts, Co or Rh complexes easily undergo metal leaching. Accordingly, supported Rh single atoms catalysts (SACs) have been recently reported to be a hopeful alternative¹. The straightforward preparation², the amenability to integrate other heteroatoms³ and the pyridine-like N presents in its structure make the g-C₃N₄ (ECN) a great candidate as catalytic support. This study comprises the design of ECN supported Rh(III) single atoms catalysts for HF. In order to study the influence of the Rh-support interaction in the catalytic stability, Rh was added through two different methods: (i) wetness impregnation (Rh/ECN) and (ii) incorporation of the Rh into the ECN structure (Rh-ECN). Highly dispersed Rh single atoms are attained through both synthesis methods (Fig 1.a), being Rh³⁺ the main species found at the surface (Fig 1.b). Eventually, the shift to lower 2θ angle compared to the bare ECN observed by XRD evidences the incorporation of Rh into its structure for Rh-ECN (Fig 1.c). Both catalysts are further tested in HF reaction of several olefins.

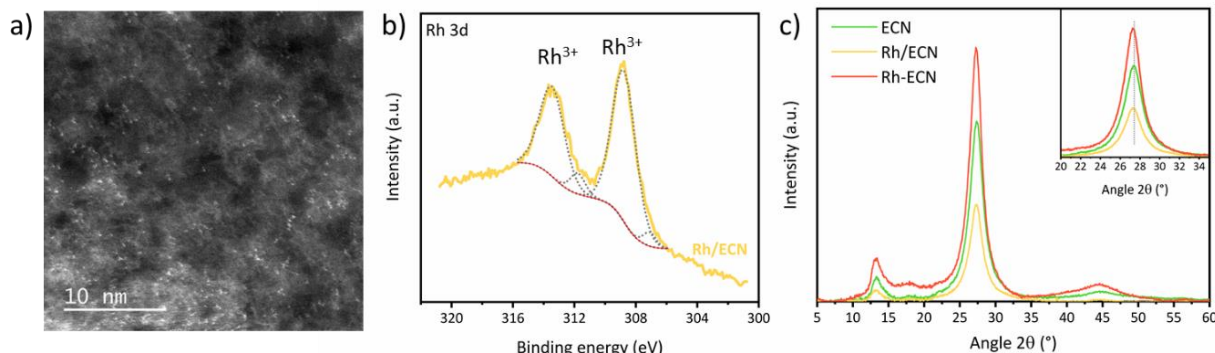


Fig 1. a) TEM image, b) XPS and c) XRD of prepared materials

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Acknowledgement: authors are grateful to the technical service of LCC, especially to Sonia Mallet-Ladeira, Jean François Meunier and Vincent Colliere. Dr Vincent César are kindly acknowledged for the support with GC analyses.

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Thematic Session: Nanochemistry and nanoparticles

Keywords: (inorganic nanoparticles, binary self-assembly, predictive approach)

Supercrystal assembly by predictive approach

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Nanoparticles have been investigated for years. A new challenge in the field consists in assembling them so as to obtain superstructures with new properties, which result from concerted effects between building blocks, and may depend on the nature of the packing (compact/sphere, porous, periodic, aperiodic, quasiperiodic, etc.). When nanoparticles are crystalline, crystals of crystals are obtained, also called supercrystals. Various examples of supercrystals have been reported in the literature, though most of them have been obtained by serendipity.

The purpose of the project is to develop a predictive and rational approach in order to synthesize nanostructured materials, by developing both theoretical and experimental techniques for determining compact packing and achieving self-assemblies of spherical nanoparticles. This work has been started focusing on the control of the size and shape of different kind of nanoparticles as well as a method to achieve to binary assemblies. A broad range of applications may be to combine their functional properties (magnetic, semiconducting, luminescent, catalytic, etc.). For example, the nanoparticles selected for that study are plasmonic (Au, Ag) and magnetic (Co, FeC, Fe₃O₄), which allow considering the origin of magneto-optical couplings in nanostructured systems.

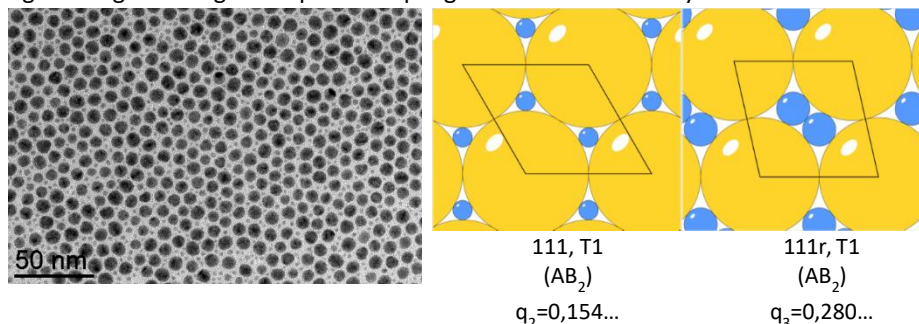


Figure 1: TEM image of binary gold nanoparticles self-assembly (left) and two of nine compact packing structures obtained by predictive approach¹ (right)

References:

1. *The nine magic ratios and the corresponding compact packings from Kennedy 2004. Figure is adapted from T. Fernique 2019*

Acknowledgment: Mission pour les initiatives transverses et interdisciplinaires - CNRS

Design, Production of Carbon Quantum Nanodots for Biotechnological Applications

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Attonuclei is a fully independent and auto-financed nanotechnology company, created a decade ago, whose mission is to perform research and develop bottom-up functionalized custom quantum dots manufacturing techniques. The company is powered by scientists with well established competence in quantum dots technology, biology, polymer chemistry, analytical chemistry, as well as computational chemistry. Our expertise lies in “Taking Theoretical and Fundamental Concepts to Commercialization” and converting high-risk ideas into high-payoff, market-based solutions with an end-to-end action.

Quantum dots are very versatile nanostructures as their size, chemical nature and surface can be tuned. They exhibit unique electronic and electromagnetic properties and used in fields such as nanobiotechnology, nanoelectronics and nanomaterials. As an example, Attonuclei has developed recently research on a new generation of photovoltaics, taking advantage of two-dimensional graphene and quasi-zero-dimensional carbon quantum dots. They both offer a large surface area, high electrical conductivity, thinness, strength and high transparency. Therefore, that represents an alternative to Si for manufacturing flexible, tiny, fast and efficient quantum dots based solar cells and FET type electronic devices.

Our mission is to create new [synergies](#) with various companies who want to improve their products, to add new functions or materials and create new innovations. Our strength is our capacity to customize functionalized Quantum Dots and engineered nanoparticles at the industrial scale.

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Thematic Session: Nanophotonics & nano-optic

Keywords: Plasmonic, Hot Electron, catalysis, Dimer, Modeling.

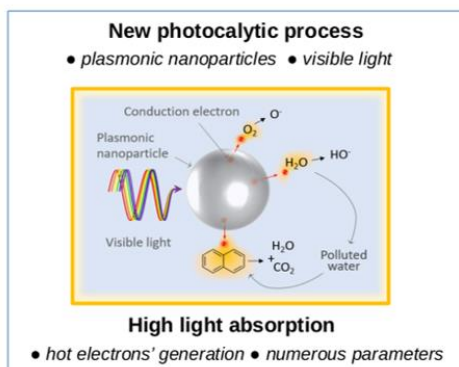
Are the hot electrons in Silver nanoparticles dimer formed near the hot spot?

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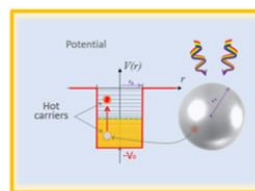
Plasmonic Hot Electrons (PHEs) have relevant and direct interests in a wide range of fields, from nanomedicine or optoelectronic to physical sensing and photocatalysis applied to chemicals production or water remediation [1]. Since the discovery of a possible direct plasmonic photocatalysis [2] various mechanisms are studied to explain this phenomenon. Some theoretical models have been developed to describe the hot electron generation by plasmonic nanoparticles [3] We propose a semi-analytical model able to describe PHEs energy and spatial distributions in the case of relatively complex geometries. In this work, we will focus on the case of the dimer of small size silver nanoparticles. We will determine if the field enhancement related to the optical dimer behavior (usually called “Hot Spot”) [4] results in an increase of the electronic spill-out and a generation of more energetic hot electrons.

1
Main objective



Electromagnetic field + absorption descriptions

- Maxwell classical laws
- Analytical / Numerical approaches



Electronic properties

- Quantum theory
- Fermi Golden Rule
- Size effect

2
Main ideas

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Acknowledgment:

We are grateful to the laboratoire PROMES CNRS, to the Occitanie Region and to the University UPVD for supports and funding.



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Thematic Session: Nanochemistry & nanoparticles

Keywords: indium phosphide, semiconductor nanocrystals, porous materials, heterogeneous catalysis.

Aerogels and hybrid materials using indium phosphide nanocrystals towards heterogeneous photocatalysis

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Colloidal semiconductor nanocrystals (or quantum dots) have attractive size-dependent optical and chemical properties that allowed them to efficiently photocatalyze many types of relevant reactions for energy conversion and organic synthesis^{1,2}. Cadmium Selenide (CdSe) quantum dots are the most famous and widely studied because of the ease of their synthesis and their high quantum yield. However, their toxicity and the prohibition of the use of cadmium in the EU have motivated the development of environmentally friendly alternatives. Indium phosphide is particularly promising thanks to its low intrinsic toxicity and theoretically emitting capacity in the entire range from the visible to the near infrared³. The main objective of this study is the development and the optimization of new synthesis methods of InP QDs from different indium and phosphorus precursors, under mild conditions compared to the routes conventionally described in the literature. Secondly, the InP QDs synthesized are confined in various kind of porous hybrid materials, with different advantages linked to their biocompatibility and high surface area in order to ensure the stability, regeneration and reuse of the InP QDs as a heterogeneous photocatalyst. For further development of the efficiency and the stability of these heterogeneous photocatalysts, functionalization of the surface of both InP semiconductor nanocrystals and the porous supports is required. We will present here different InP QDs candidates as photocatalysts and a first series of hybrid materials incorporating these QDs.

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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.

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Thematic Session: Nanochemistry and nanoparticle

Keywords: Nanocrystals, indium phosphide, indium amidinate

Indium amidinate as a novel precursor for the synthesis of indium phosphide nanocrystals

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The synthesis of indium phosphide nanoparticles has been an active research topic for thirty years^[1]. The most common synthesis route involves the reaction of indium carboxylate and tris(trimethylsilyl)phosphine at high temperature (>230°C). However, the use of high temperatures results on one hand, in the partial oxidation of the surface nanoparticles and on the other hand, in a lack of growth control and broader emission^[2]. In this poster, I will show that the replacement of indium carboxylate by a novel indium precursor allows the formation of InP nanoparticle at record low temperature (150°C) and therefore prevent the surface oxidation even in the presence of O-containing ligands^[3].

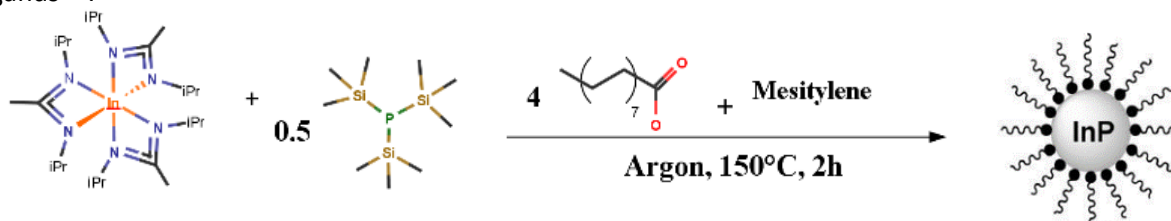


Figure 1: Reaction scheme of InP synthesis with the Indium amidinate

The study of the mechanism will be presented and the influence of the second sphere of coordination of semiconductor NCs on the growth processes will in particular be highlighted.

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[3] Synthesis of Oxide-Free InP Quantum Dots: Surface Control and H₂-Assisted Growth. Baquero, E.; Virieux, H.; Swain, R.; Gillet, A.; Cros-Gagneux, A.; Coppel, Y.; Chaudret, B.; Nayral, C.; and Delpech, F. *Chemistry of Materials* **2017** 29 (22), 9623-9627. DOI: 10.1021/acs.chemmater.7b04069

Acknowledgment: Agence National de la Recherche ANR-18-CE09-0039

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Thematic Session: Nanochemistry and nanoparticles

Keywords: Metallic nanoparticles, interfacial chemistry, colloids, Ouzo emulsion.

Synthesis of metallic nanoparticles at the liquid/liquid interface in Ouzo type emulsions

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In this work, nano-objects composed of metallic nanoparticles (NPs) synthesized by an interfacial reaction in an Ouzo-type emulsion are investigated. The Ouzo phenomenon happens when two miscible liquids are initially mixed together in certain proportions. Then, the addition of an impurity, miscible in only one of the two liquids, forces phase separation. In our case, tetrahydrofuran (THF) and water are used in the presence of butylated hydroxytoluene (BHT) – a stabilizer added to THF. We take advantage of this instantaneous emulsion for the interfacial redox synthesis of nanoparticles: a reducing agent is added to the aqueous phase (NaBH_4) and a metallic precursor (AuPPh_3Cl) is added to the organic phase (THF). When the liquids are mixed, THF/BHT droplets containing the precursor are formed in the aqueous phase containing the reducing agent, initiating the redox reaction. This leads to the *in situ* formation of NPs at the THF/water interface. Transmission electron microscopy (TEM) analysis (imaging and energy dispersive X-ray spectroscopy) revealed the formation of nano-objects formed by closely packed AuNPs, as seen in Figure 1a. This synthesis approach is straightforward, versatile and compatible with an array of metallic precursors (*e.g.* gold or palladium – Figure 1b), and their combinations. These nano-objects may open possibilities in the fields of catalysis, chemical sensing, and imaging, amongst many other applications.¹⁻²

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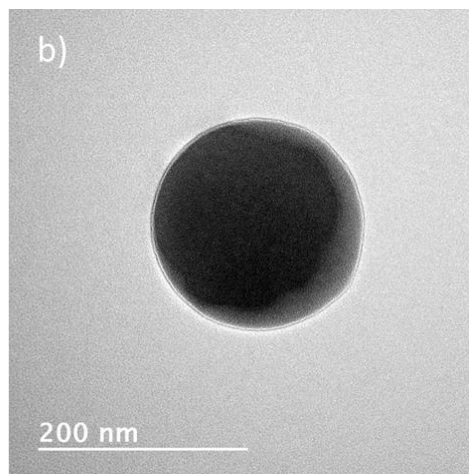
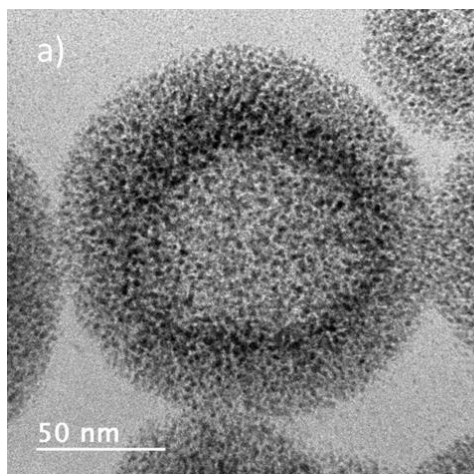


Figure 1. TEM micrographs of spherical nano-objects synthesized with gold (a) and palladium (b) precursors.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: Ouzo domain, nanoparticles, phase diagram, Quantum Dots, SPION, SFME domain

Understanding the “Ouzo effect” and the influence of Nanoparticles in Ouzo systems

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The “Ouzo effect” is a spontaneous formation of a metastable and monodisperse emulsion, without using surfactant or external energy input.¹ This phenomenon occurs when a water-miscible solvent containing a hydrophobic compound is mixed with a large amount of water. It results in the supersaturation of the hydrophobic compound and the formation of solvent-rich droplets. The Ouzo effect has been used to nanoprecipitate and nano-encapsulate drugs for controlled delivery.² Moreover, a domain called Surfactant-free microemulsion (SFME) exists in a large part of the monophasic region and is described as a spontaneous formation of stable microemulsions, also without using surfactant nor energy.³ The size evolution of nano-objects obtained in SFME and Ouzo domains has already been studied by Dynamic Light Scattering (DLS) analysis for the miglyol/acetone/water system.⁴ Our work focuses on a more detailed understanding of the Ouzo domain and the transition between the SFME and Ouzo domains within a model ternary system (limonene/DMSO/water). We used DMSO as solvent for biological applications. In previous studies, the phase diagrams are investigated using DLS. In our work, we used Nanoparticle Tracking Analysis (NTA) which gives more realistic information on the size distribution of the dispersed phase (in the range 50 nm-1 μ m) and its concentration in the sample. We compared our NTA results to those obtained by DLS. We also studied the influence of inorganic nanoparticles (Iron oxide, Quantum Dots; \sim 5 nm) on the phase diagrams of “Ouzo systems”. We found that the addition of nanoparticles can change the limits of the Ouzo domain, the size and concentration of the resulting nano-objects. As a general rule, nanoparticles stabilize droplets formed by the Ouzo effect.

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³ R. E. Barden *et al.*, *J. Colloid Interface Sci.*, **1977**, 60, 488-496

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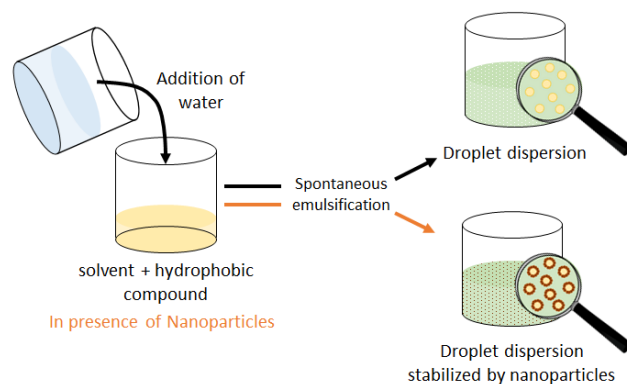


Figure 1 : Schematic representation of the “Ouzo effect” principle

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: metal nanoparticles, ruthenium, nickel, palladium, organometallic chemistry, controlled structure, catalysis

Molecular Chemistry Tools for the Rational Development of Nanocatalysts

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Catalysis is one of the major themes in chemical landscape. Since a few decades, nanocatalysis, which lies at the interface between homogeneous and heterogeneous catalysis, proved to offer very promising results. Nanocatalysts may present properties of both heterogeneous catalysts (stability, recyclability, scalability) and of the homogeneous ones (activity, selectivity)^[1]. However, despite the wide progresses in nanochemistry observed in the last two decades, a better understanding of the relationships between the structural characteristics of the nanomaterials and their catalytic performance is still needed. Model nanocatalysts are thus required to study fundamental processes that occur at their surface with the aim to design more efficient catalysts^[2]. In this context, the concepts of molecular chemistry are very beneficial and allow developing efficient synthetic tools^[3]. Organometallic complexes are suited precursors to provide well-controlled metal nanoparticles in terms of size, shape, composition, chemical order for bimetallics and dispersion, key-parameters for any target application as catalysis^[4]. By choosing the adequate system, it is possible to have at disposal model nanoparticles in order to study the effect of their architecture, structure and surface state onto a given reaction.

We will here present the organometallic synthesis of mono and bimetallic nanocatalysts composed of ruthenium, nickel and palladium. Their structural characterization will be discussed, always keeping in perspective the potential impact over the catalytic application.

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Acknowledgment: ANR PRECINANOMAT n°: 17-CE06-0017

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: nanodiamond, surface modification, solvated electrons

Surface modifications of detonation nanodiamonds and overproduction of hydroxyl radicals and solvated electrons under irradiation

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Among nanocarbons, detonation nanodiamonds (DNDs) present interesting chemical and physical properties for a wide range of applications. Our recent studies demonstrated that under ionizing radiation (X and gamma rays), overproductions of hydroxyl radicals (HO^\bullet) and solvated electrons (e^-_{solv}) are observed in the presence of hydrogenated DNDs suspended in water^{1,2}. These species constitute powerful chemical oxidizing and reducing agents that open the way to new applications, especially in photocatalysis (CO_2 reduction into exploitable compounds) or in nanomedicine (radiosensitization of cancerous cells). Since no overproduction is observed for oxidized DNDs, the surface chemistry appears to be of primary importance. Surface hydrogenation is achieved either by hydrogen plasma or by annealing under hydrogen, leading to carbon/hydrogen terminations. Nevertheless, Raman and HRTEM investigations show the presence of some graphitic reconstructions.

The aim of this study is to better understand the specific role played by graphitic reconstructions and hydrogen terminations in the overproduction of HO^\bullet and e^-_{solv} . For this purpose, more refined treatments of DNDs are performed to produce gradual stages of surface graphitization. The surface chemistry of each sample is deeply characterized (FTIR, Raman, XPS) to evaluate its hydrogen and sp^2 content. Concentrations of HO^\bullet are indirectly measured using fluorescent coumarin probes. Actually, fluorescent quantification of e^-_{solv} via coumarin probe needs degassing and can't be applied to any kind of sample. Therefore, another objective of this work is to develop an alternative protocol of quantification of solvated electrons by fluorescence, sensitive enough and compatible with DNDs.

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P5 - MULTIFUNCTIONAL NANOCOMPOSITES

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Thematic Session: Multifunctional nanocomposites

Keywords: Dielectric barrier discharge, Pulsed injection, atmospheric pressure, Hexamethyldisiloxane (HMDSO), thin film, FTIR

Effect of pulsed precursor injection on the deposition of pp-HMDSO thin film in a Dielectric Barrier Discharge

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Abstract

Nanocomposite (NC) thin-films are widely studied due to the multifunctional properties they can develop (optical, electrical, mechanical, chemical, biological).

A lot of methods are under development with a real attention to aerosol-assisted plasma processes at atmospheric pressure, such as dielectric barrier discharge (DBD) [1]. Nebulization of colloidal solutions have been previously used. However, the nanoparticles embedded in the matrix are found aggregated [2]. Recently, a reactor-injector of nanoparticles has been developed [3]. This new method consists in synthesizing the nanoparticles prior to their injection in the plasma in a pulsed injection regime.

This work aims to study the impact of a pulsed injection in a DBD. In contrast with the continuous nebulization of solutions, pulsed injection causes a sudden increase of the quantity of precursor in the inter-dielectrics space. When using liquid precursor, it consists in droplets. We examined the effect of time injection on the discharge stability and on the thin film deposition. It is shown that this pulsed injection plays a very critical role on the formation of plasma polymerized coatings.

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Thematic Session: Nanochimie & Nanoparticules

Keywords: Ionic liquids, block copolymers, self-assemblies, thermoresponsive

Doubly thermo-responsive copolymers in ionic liquid

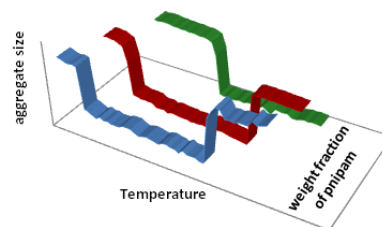
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Abstract

Room temperature ionic liquids (IL) are tunable and generally environmentally benign solvents that enable to tackle scientific challenges for the industrial implementation of green innovations. Of peculiar interest are composites made of ILs and polymers that have opened new challenges in polymer materials science.⁽¹⁾ Many studies have aimed at understanding the solubility and the phase behavior of various polymers in ILs.⁽²⁾ Whereas some polymers exhibit a lower critical solution temperature (LCST), others present an upper critical solution temperature (UCST). For example, poly(N-isopropylacrylamide) (PNIPAM) exhibits a LCST in water, it presents an UCST in an hydrophobic IL [C₂mim][NTf₂].⁽³⁾

In this study, we focus on colloidal systems obtained by the assembly of thermoresponsive block copolymers within [C₂mim][NTf₂]. Different series of well-defined poly(n-butylacrylate)-*b*-poly(N-isopropylacrylamide) diblock copolymers were synthesized by RAFT/MADIX polymerisation. Their solution behavior in [emim][NTf₂] as a function of temperature was investigated by scattering and turbidity techniques. These polymers exhibited a doubly thermo-responsiveness with an UCST and a LCST. For a given molar mass, these temperatures can be easily controlled by choosing the PBA to PNIPAM balance or by altering the polymer composition of the PNIPAM block by insertion of an additional comonomer. Interestingly, these transitions are accompanied by strong modifications of the polymer morphology in solution and a switch from micellar to reverse micellar structures is observed. This property can be used to develop reversible shuttles between ionic liquid and water, the transfer temperature of which can be easily tuned by the proper choice of the polymer structure.



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Thematic Session: Nanophotonics & nano-optics, nanomaterials, nanoparticles

Keywords: photomodulation, holographic grating, photochromism, magnetism

Toward the photofabrication of functional nanoarchitectures

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In order to create optically and magnetically activatable memory devices, a strategy is to promote the organization of functional nanoparticles on photoactive surfaces, generating a higher density of stored data. Thus, we can expect higher performance than those obtained with massive materials..

The first step of this work involves the synthesis of photochrome azo molecules with bulky groups to facilitate solid-state photochromism and a complex group for chelating metal oxide nanoparticles. [1] Superparamagnetic nanoparticles such as magnetite are synthesized by thermal decomposition of metal complexes. We are interested in nanoparticles that differ in size and morphology. Attention is paid to the absence of aggregation between nanoparticles and to "monodomain" magnetic characteristics, imposing sizes of less than 25-30 nm (Figure 1a). [2]).

The organization of nanoparticles is based on a method of holographic inscription on thin molecular films made exclusively from azo molecules. Under structured light irradiation, photochrome molecules undergo a photoisomerization reaction leading to a matter transport throughout the sample. Surface networks are then formed in a reversible and controlled height (Figure 1b). The association of magnetic nanoparticles with organic surface networks must lead to their organization.

We were thereby interested in the different ways in which superparamagnetic nanoparticles can be integrated into the organic matrix and the affinities they can develop with the azo material depending on their surface functionalization (Figure 1c).

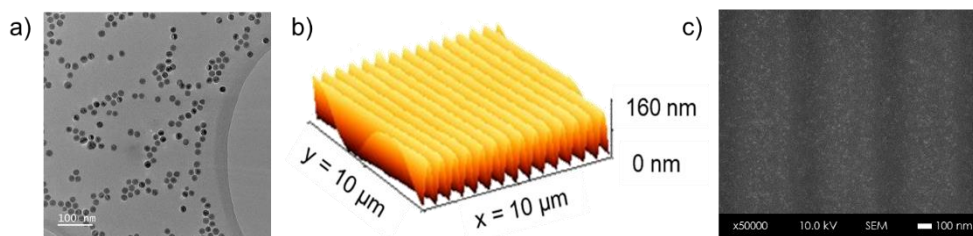


Figure 1 : a) TEM image of iron oxide nanoparticles (x55000). Surface network of AzoEster (polarization +45°/-45°, $\lambda_{exc} = 488 \text{ nm}$, $P_{irr} = 240 \text{ mW/cm}^2$; b) AFM image of a network without particles ; c) SEM image of a network with iron oxide nanoparticles.

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Thematic Session: Nanochemistry & Nanoparticles

Keywords: AFM, mechanochemistry, single-molecule studies, nanomachines

Tying a synthetic molecular knot in solution using an atomic force microscope

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Mechanically interlocked molecules (MIMs), such as rotaxanes, catenanes and molecular knots, have attracted a lot of attention in the past years for the design of artificial molecular machines. Unique properties can arise from these molecules, originating from the presence of mechanical bonds in their architectures. Their use as molecular switches, machines, or motors has been intensively discussed in the literature. The mechanochemical properties of individual MIMs have been studied using single-molecule techniques such as atomic force microscopy (AFM) or optical tweezers.¹⁻⁴

Here we show the first example of AFM-based pulling experiments on artificial molecular overhand knots at the single-molecule level. The synthesis⁵ of a trefoil knot —the simplest prime knot— was modified to facilitate its interfacing for AFM experiments. Standard SMFS experiments on individual overhand knots evidenced force deviations from the usual force-extension curves of flexible polymers. Characteristic force increases were observed repeatedly at pulling extensions similar to the total PEG length, thus indicating a mechanical tension applied to the knotted part of the molecule. Precise measurements of the length revealed after these deviation features helped uncovering the mechanically-induced tying pathway.

Such challenging studies are essential to understand the impact of mechanical bonds on the properties of wholly synthetic architectures and are crucial for further uses of MIMs in the design of functional materials.

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Acknowledgments

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Thematic Session: multifunctional nanocomposite

Keywords: nanocomposite, Ag nanoparticles, thin dielectric film, dielectric permittivity, Electrostatic Force Microscopy

A multiscale investigation of nanocomposite dielectric permittivity: application to plasma deposited AgNPs-based nanocomposites

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Abstract

Thin nanocomposite dielectric films, with tuneable electrical properties, appear convenient for the development of reliable and performant micro- and nano-devices. In this context, nanocomposites based on silver nanoparticles (AgNPs) are attractive due to their multifunctional properties which address applications from biocide treatment [1] to energy [2]. For optimization purposes, their electrical properties and behaviour under electrical stress need to be probed from macroscale to nanoscale. Concerning nanoscale, electrical modes derived from Atomic Force Microscopy appear as the best way. Indeed, Conductive AFM (C-AFM), Kelvin Probe Force Microscopy (KPFM) or Electrostatic Force Microscopy (EFM) have previously been exploited to determine leakage current in gate oxide, charge at oxide/semiconductor interface in MOS devices or dielectric permittivity in composite thick layers [2-4].

In this work, we focus on the dielectric permittivity properties of thin dielectric silica layers with embedded AgNPs. Their structure comprises a single AgNPs layer inserted at well-controlled distance from the SiO₂ surface [2, 5]. The dielectric permittivity is probed at macroscale using impedance spectroscopy and at nanoscale using EFM [4-5]. To compare the results and understand the influence of metal inclusions on the dielectric permittivity of silica, a Finite Element Modelling is used. The nanocomposite apparent dielectric permittivity increases when the AgNPs plane is close to surface (less than 20nm). However, the permittivity varies locally depending on the position of the AFM tip: facing a AgNP or placed between two AgNPs. This is related to screening effect induced by the AgNPs. This effect can be anticipated based on electrostatic modelling.

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Thematic Session: Nano for Imaging, diagnosis and therapy

Keywords: Smart microgels, gold nanoparticles, fluorescence probes, photoacoustic imaging, Raman imaging, phototherapy

Versatile Design of Multifunctional Microgels from Molecular, Nano- and Microscale Building Blocks for Biomedical Applications

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Abstract. The development of hybrid microgels based on the integration of inorganic nanoparticles into polymeric particles has stimulated worldwide efforts in recent years due to their promising biomedical applications as smart therapeutic system and bioimaging agents^{1,2}. In this talk, we describe an innovative modular strategy to obtain multifunctional smart hybrid particles based on the self-assembly of different building blocks (stimuli-responsive microgels, gold nanoparticles and fluorescent dyes) that could be compared to the assembly of lego® bricks (Fig. 1). The final hybrid networks display intense Raman signatures due the presence of the gold nanoparticles (Au NPs) trapped within the polymer matrix, which strongly enhance the vibrational signals of the dyes. The nanohybrids thus act as surface-enhanced Raman spectroscopy (SERS) tags for bioimaging. Moreover, the Au NPs trapped within the particles are also valuable light-to-heat plasmonic converters for biomedical hyperthermia. Besides, the combination of both Au NPs and dyes offers

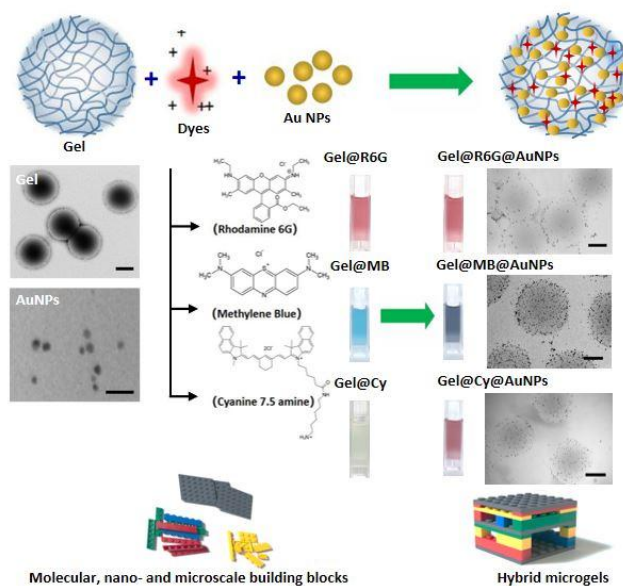


Figure 1. Smart combination and assembly of cationic molecular linkers (fluorescent dyes), negatively charged inorganic NPs (Au NPs) and polyanionic microgels. Scale bar = 200 nm except for AuNPs (scale bar = 20 nm).

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added-value property for photoacoustic imaging. Such hybrid particle thus not only combine the remarkable physico-chemical features of each component but also display synergetic properties that open promising prospects for a broad range of biomedical applications, including photoacoustic, Raman imaging and phototherapy.

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Session: Multifunctional nanocomposites

Efficient doping of highly doped thin SOI layers by Laser Thermal Annealing processes

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The appearance of localized surface plasmon resonance in highly doped Si nanocrystals (NCs) has opened a new field of applications for Si [1]. However, doping nano-Si remains a challenge due to self-purification effects [2]. If most of the highly doped Si-NCs are elaborated by bottom up processes [1], new routes involving top down approaches, as low energy electron lithography of heavily thin doped SOI wafers, can be appealing. In this case, a prerequisite step consists in the optimization of the top Si layer doping process.

In this work, a thorough study of the doping of SOI wafers is described. UV nanosecond laser annealing (UVNLA) is used to achieve an efficient dopant activation [3]. 23 nm thick SOI top Si layers have been implanted with phosphorus at 4 keV for dopant concentrations ranging between 1 and 10 at.% and LTA conditions leading to the full melting of the implanted layer. The recrystallisation processes and P redistribution in the Si layer have been investigated as a function of the laser energy density by STEM-HAADF/EDX. A pile-up of P atoms at the surface has been observed, which increases with the implant dose. For optimised LTA conditions, complete re-crystallisation and reduced sheet resistance values have been achieved, with active dopant concentrations as high as 4 at. % measured by Hall effect and deduced from FTIR measurements coupled with Drude model-based calculations.

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Keywords: Silicon-On-Insulator, laser thermal annealing, recrystallization, dopant activation, STEM

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Thematic Session: Multifunctional nanocomposites

Keywords: Polymers, nanocomposites, nanoparticles, electro-optic effect, optical properties

Electro-optic nanocomposites for high performance microwave photonic applications

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Abstract

Great interest is devoted to electro-optic (EO) polymers since they allow the fabrication of very high performance microwave photonic components with a higher EO coefficient than the very popular inorganic LiNbO_3 EO material [1]. EO polymers are composites of a polymer matrix and chromophores. The chromophores confer the macroscopic EO effect after alignment by poling, usually by heating the polymers near their glass transition temperature and applying a very high DC electric field, taking advantage of the polarizability of the chromophore molecules. In this work we are interested in guest-host systems where PMMA (poly(méthacrylate de méthyle)) is used as matrix and DR1 (Disperse Red One) as chromophore. We study the influence of nanoparticles (NP) loading on optical properties of EO polymers. Our first study focuses on PMMA-DR1 polymer loaded with TiO_2 NP which we expect to allow obtaining a nanocomposite of higher EO performances than those of the raw PMMA-DR1 polymer. Experimentally, we have optimized the NP dispersion process, the deposition protocol and some physical characterizations in order to obtain homogeneous and smooth 3- μm thick films of which we know precisely the chromophore content. The **M-lines technique** measures an increase of the refractive index at telecom wavelengths of 1.3 and 1.55 μm after addition of 1 or 2 wt% of TiO_2 NP. Alignment of the chromophores is obtained after poling as attested by the presence of a SHG (Second Harmonic Generation) signal, which remains stable over 2 months. However the loading with TiO_2 NP influences the poling process and its efficiency. An electrostatic model in COMSOL was made to understand possible effects of adding NP on the poling process and its efficiency. We discuss all these results in this paper.

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P6 - NANOMATERIALS FOR ENERGY

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Thematic Session: Nanomaterials for Energy

Keywords: Zeolite-Templated Carbon, energy storage, supercapacitor, microporous carbon, Chemical Vapor Infiltration

Zeolite-Templated Carbon : a Promising Material for Supercapacitors

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Chemical vapor infiltration (CVI) of a hydrocarbon in a molecular sieve is a synthesis technique used to generate a crystalline structure of carbon that remains up to now purely theoretical: Schwarzite [1-2]. This structure has indeed been foreseen as a promising material to manufacture electrodes for supercapacitors. Nonetheless, many technological challenges still have to be overcome in order to make this synthesis technique more accessible [1].

The molecular sieve that was selected for this study is zeolite, for its extraordinary adsorption properties. Zeolite is used as a template: the aim is to replicate its structure by infiltrating carbon atoms inside the nanopores [3]. The idea is to obtain, after zeolite dissolution by means of hydrofluoric acid treatment, a material that is exclusively composed of carbon, with a 3D porosity network consisting of nano-sized pores and thus displaying a high specific surface (see figure1).

SEM observation shows that the obtained material has a very similar structure to that of the initial zeolite (see figure 2) which augurs well for the successful replication of the zeolite structure.

Therefore, the presentation will focus on the synthesis and characterization of these materials, using thermogravimetric analysis, X-Ray diffraction, Raman, etc.

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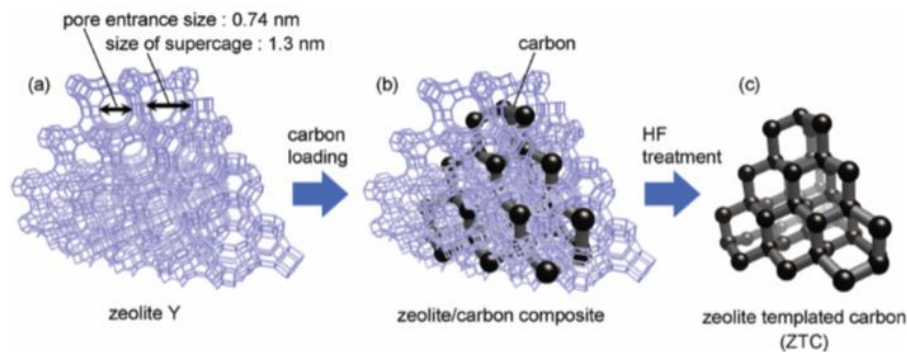


Fig. 1 : Schematic Zeolite-Templated Carbon (ZTC) Synthesis [3]

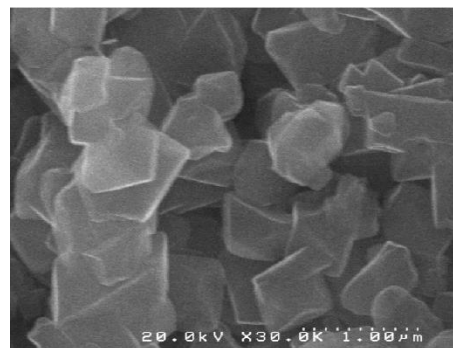


Fig. 2 : SEM image of carbon material obtained after zeolite dissolution with hydrofluoric acid

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Thematic Session: (Nanomaterials for Energy)

Keywords: (Electrocaloric effect, Thermoreflectance, solid-state cooling)

Characterization of electrocaloric thin films via Frequency-Domain ThermoReflectance

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Vapour compression techniques have dominated the design of refrigeration and air conditioning systems so far. Although these systems are efficient, they come with extreme downsides, global warming, ozone depletion, and vibrations... Thus, international protocols have regulated harmful refrigerant¹. There has been increasing interest in novel refrigeration techniques to expand the benefits of artificial cooling.

Electrocaloric effect (ECE) is the isothermal entropy or adiabatic temperature change of a dielectric material when an electric field is applied or removed. When an electric field is applied to a polar material, it will induce a change in the material's polarization. ECE could provide an efficient means for the realization of solid-state cooling devices for a wide range of applications, such as on-chip cooling and temperature control for sensors and electronic devices, given that large ECE materials can be produced. Refrigeration based on the ECE approach provides an eco-friendly, alternative to the current techniques^{2,3}.

To obtain an efficient cooling system, current research is moving towards stacks of thin layers with nanometric thicknesses. The thickness, density, thermal conductivity, and electrical conductivity of these films are all critical parameters⁴. Thermoreflectance is an optical pump-probe technique effectively used for thermal characterization of thin films at the submicrometric scale because it has a high resolution, comparable to the wavelength of the beams⁵. In this study, the pump laser is replaced by the electric field applied into our sample, and variations of its temperature will be probed by a 660 nm wavelength laser diode.

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Thematic Session: Nanomaterials for Energy

Keywords: Micro Solid oxide cells (μ -SOFCs), cathode, thin film growth, oxygen reduction reaction, electrical conductivity relaxation

Understanding the origin of the enhanced activity of L2NO4 micro-SOFC cathodes at low temperatures

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Energy conversion and storage systems based on solid oxide fuel cells (SOFCs) are promising candidates for future power solutions due to their high efficiency, low cost, hazard-free and sustainable material components¹. Miniaturisation and portabilisation, however, requires lower operation temperatures, linked to decreased electrochemical performance and increased polarization resistance, with sluggish cathode surface activity being the major source.

In this study we investigate the Ruddlesden-Popper phase La_2NiO_4 (L2NO4), a highly interesting electrode material for intermediate temperatures, due to its low activation energy of the surface exchange activity², a prerequisite for the operation of micro-SOFCs at $\leq 500^\circ\text{C}$. By growing L2NO4 thin films by pulsed injection Metalorganic Chemical Vapor Deposition (PI-MOCVD) on various substrates and with different thicknesses (tens to hundreds of nm) we were able to tune the strain and film orientation and analyze its effect on the oxygen exchange activity. We achieved very high surface exchange coefficients and low area specific resistance (ASR) values at low temperatures (400-500°C) when compared to other cathode materials, as measured by electrical conductivity relaxation (ECR) and electrochemical impedance spectroscopy. Microstructure and morphology are characterized by XRD, SEM, AFM, etc. The oxygen incorporation is directly addressed using ECR measurements under specific well defined methodology which allowed us to identify for the first time the rate determining step in L2NO4 thin films. Finally, we propose new strategies to further enhance the electrochemical performance of this promising cathode material.

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December, 8, 9 and 10



Thematic Session: *Nanomaterials for Energy*

Keywords: Layered chalcogenides; Thermoelectrics; Thermal transport; DFT; Boltzmann transport

DFT investigation of electronic and thermal transport properties in $\text{Pb}_2\text{Bi}_2\text{Te}_5$

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Chalcogenide compounds such as PbTe , PbBi_2Te_4 , PbBi_4Te_7 and Bi_2Te_3 that belong to the homologous series of ternary phases $n(\text{PbTe})\cdot m(\text{Bi}_2\text{Te}_3)$, exhibit both excellent topological insulators and promising thermoelectric properties [1,2]. For $2(\text{PbTe})\cdot(\text{Bi}_2\text{Te}_3)$ also read as $\text{Pb}_2\text{Bi}_2\text{Te}_5$, two different possible atoms sequences have been reported: $-\text{Te-Pb-Te-Bi-Te-Bi-Te-Pb-Te}-$ (S1) and $-\text{Te-Bi-Te-Pb-Te-Pb-Te-Bi-Te}-$ (S2). We have performed a series of first principles calculations using density functional theory (DFT) to determine electronic and thermoelectric properties of $\text{Pb}_2\text{Bi}_2\text{Te}_5$ with these 2 different atoms sequences. The related compounds PbTe and Bi_2Te_3 have also been investigated for comparison. Different exchange-correlation functionals (LDA, PBE, EV, TB-mBJ potentials, and rev-vdW-DF2) have been tested, w/o spin-orbit coupling, which has been found to have important effects. The calculated electronic bands indicate that both the 2 sequences lead to indirect band gap semiconductors. We also have calculated elastic moduli, dielectric constants, Born effective charges, and phonon dispersion within the quasi-harmonic approximation. Based on the above-mentioned calculations results, thermal conductivity has been obtained by solving the Boltzmann transport equation. The most interesting compound for thermoelectric applications has been found to be $\text{Pb}_2\text{Bi}_2\text{Te}_5$ with the S2 sequence.

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Thematic Session: Nanomaterials for energy

Keywords: Polytype, Nanowire, Monte Carlo, Thermal, Simulation

Monte Carlo study of thermal transport in polytype nanowires for thermoelectric applications

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Interfaces can be used to design low thermal conductance nanostructures to achieve optimized thermoelectric performance. Polytype nanowires [1], [2] which can be fabricated in silicon or germanium are particularly attractive for thermal engineering as they can exhibit a high interface density.

In this work, we theoretically study the thermal transport of phonons across the polytype heterojunction Si 3C/Si 2H by using particle Monte Carlo simulation [3] to solve for the Boltzmann transport equation for phonon. It includes a full-band phonon dispersion and phonon-phonon scattering rate in each material calculated by using the density-functional theory (DFT). Both rough interfaces and semitransparent interfaces modelled by the diffusive mismatch model are considered. The variation of the interface thermal conductance as a function of the geometric dimension as well as the effects of the orientation are studied.

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Screening of the synthesis route on the structural, magnetic and magnetocaloric properties of $\text{La}_{0.6}\text{Ca}_{0.2}\text{Ba}_{0.2}\text{MnO}_3$ manganite: A comparison between solid-solid state process and a combination polyol process and Spark Plasma Sintering

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abstract

$\text{La}_{0.6}\text{Ca}_{0.2}\text{Ba}_{0.2}\text{MnO}_3$ ceramics are prepared by an original route, combining soft chemistry and Spark Plasma Sintering, within a few minutes at 700 °C and by the solid-state reaction at high temperatures with an annealing temperature of 1200 °C. We have studied the leverage of the powder synthesis method on the structural, morphological, magnetic and magnetocaloric properties of the samples. X-ray diffraction analysis using Rietveld refinement revealed that our materials crystallize in the rhombohedral system with R3-c space group for the sample prepared by the Polyol-Spark Plasma Sintering method and in the orthorhombic structure with Pbnm space group for the sample synthesized by the solid-state reaction. Magnetization measurements versus temperature under magnetic applied field of 0.05 T show a paramagnetic-ferromagnetic phase transition for both samples. The Arrott plots reveal that our materials undergo a second-order phase transition. The maximum values of the magnetic entropy change ($-\Delta S^{\text{max}}_{\text{M}}$) under the magnetic field change of 5 T are 2.4 and 4.7 J/kg K for $\text{La}_{0.6}\text{Ca}_{0.2}\text{Ba}_{0.2}\text{MnO}_3$ synthesized by using solid-state reaction and Polyol-Spark Plasma Sintering methods respectively. The highest value of the relative cooling power RCP is found to be 244 J/kg for the Polyol-Spark Plasma Sintering sample under 5 T. These results are interesting enough and suggest that the Polyol-Spark Plasma Sintering synthesis method is a feasible route to prepare high quality perovskite material for magnetic cooling application.

Keywords: Manganites, Preparation methods, Magnetization, Magnetocaloric effect

- Mobile Number*: +12658621003
- Category*: Oral presentation
- WhatsApp No: +12658621003
- Research Interest*: Magnetic Materials



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Thematic Session: nanomaterials

Keywords: ($\text{CuIn}_{1-x}\text{Fe}_x\text{Se}_2$ – solvothermal – chalcopyrite - powders)

Syntheses and characterizations nanoparticl of $\text{CuIn}_{1-x}\text{Fe}_x\text{Se}_2$ chalcopyrite

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Abstract

$\text{CuIn}_{1-x}\text{Fe}_x\text{Se}_2$ powders with different atomic percentages (x) were prepared with the solvothermal method. The experiment aims to study the effect of atomic percentages of Fe_x on the physical properties of $\text{CuIn}_{1-x}\text{Fe}_x\text{Se}_2$ in order to enhance future technological applications based on this material. The chalcopyrite phase and the grain size of the powders were determined by XRD. EDX analysis reveal the existence of Cu, In, Fe and Se with the adequate atomic ratio of Fe/ (In + Fe). SEM and TEM analysis exhibit that the powders have large-scale desert-rose-like structures. The powder optical study by UV-visible spectrophotometry shows that the values of the gap energies of $\text{CuIn}_{1-x}\text{Zn}_x\text{Se}_2$ increase with the molar fraction of Fe_x from 1.15 to 1.5.

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Thematic Session: Nanomaterials for Energy

Keywords: Solar energy, Metamaterial, Black absorber, Steam generation, Optimization

Optimization of porous metamaterials for enhanced solar steam generation

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Solar surface steam generation is a promising technology for water purification using renewable energy resources¹. In recent years, in order to effectively absorb and use solar energy, nanomaterials as black silicon² and black TiO₂³ have been developed and characterized. As the evaporation only occurs at the air-water interface, steam generation efficiency can be increased by localizing the heating process at this interface and reducing the water reservoir bulk heating using porous black absorbers. Consequently, the black absorbers need to combine optimized radiative properties, a large absorptivity of the solar spectrum for instance, and an optimized porosity to enable capillary water transport and surface water evaporation. In this work, we report on numerical simulations of surface-enhanced solar steam generation to optimize the solar steam generation rate. Numerical simulations are performed using commercial multi-physical simulation tools (Comsol Multiphysics) to reveal the effect of key materials properties such as the absorptivity, porosity and thermal conductivity on the evaporation rate. An optimal porosity of 0.75 is found to maximize the steam generation rate. We also report on the observed trend of the steam generation rate with respect to other governing materials properties. Preliminary experimental results are also reported using a porous metamaterial based on black silicon.

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P7 - NANO HEALTH ENVIRONMENT & RISKS

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Thematic Session: Nano: health, environment & risks

Keywords: Carbon nanomaterials; Antimicrobial; Composites; Polymer

Antimicrobial applications of carbon-based polymer-matrix nanocomposites

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Carbon Nanomaterials have been widely studied and present many exceptional properties, including antimicrobial properties. Their incorporation into materials to confer them antimicrobial properties has generated a growing interest with an increase in number of publications since 2011 [1, 2]. The use of a polymer matrix presents many advantages, as polymers proved to be both efficient nanoparticle holders and also demonstrate intrinsic antimicrobial properties in some cases [3].

The state of the art of the fabrication methods of such antimicrobial materials, the main antimicrobial tests used, and the proposed antimicrobial mechanism will be presented, along with potential applications. Even if many examples of such composites are found in the literature, there is still a lack of information concerning the occurring antimicrobial mechanism. Moreover, there are currently no clear conclusions regarding toxicity aspects or possible release of particles from these materials.

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Thematic Session: Nano: health, environment & risks

Keywords: carbon nanotubes, *Physarum polycephalum*, cytotoxicity, internalization

Impact of carbon nanotubes on an emerging cellular organism: *Physarum polycephalum*

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Abstract:

Carbon nanotubes (CNTs) are a category of nanomaterials with applications in all fields (energy, transports, composite materials and environment) due to their exceptional mechanical, optical and electronic properties. However, their use should depend on the non-toxicity of these nanomaterials, and little is still known on their impact on living beings^{1,3,4}. This study evaluated the toxicity of double-walled carbon nanotubes (as a model of CNTs in general) on the unicellular organism *Physarum polycephalum*, which, due to its simplicity of organization and behavioural complexity², is a model of choice. The objective was to assess the fate of CNTs within the cell of *Physarum polycephalum*, and to evaluate their impact on the behaviour of the latter. For this purpose, organisms were contaminated along three routes of exposure (topical, food, environment) in order to determine the internalization of CNTs. Accumulation, persistence and excretion of CNTs within the cell were then assessed only by food exposure of the organism. From a behavioural point of view, impacts on the migration speed and the early growth (pseudopod appearance) were also investigated.

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Thematic Session: (Nano: Health, Environment and Risks)

Keywords: (Brake, Particles, Toxicity, Characterization)

Chemical and Mössbauer Spectroscopy Characterization associated to Oxidative Potential of particulate matter from Brake Wear Emissions

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The road transport is recognized to be an important contributor to the air pollution. Brake wear may contribute up to 55% in mass of PM₁₀ of total emission of non-exhaust particles. The presence of high content of heavy metal and their oxides (Kukutschova *et al* 2011) in brake dusts combined to a nanosized fraction predict of their cytotoxic effects and oxidative stresses (Gasser *et al* 2009). We report chemical characterization of brake wear using TEM/STEM-EDX single particle analysis, to identify chemical element size and morphology of particles, known to be key determinant in tissue interaction or cellular uptake (Buzea *et al* 2007). Particles were generated from a home-made bench test designed specifically to reproduce real-world driving conditions. Source of many health adverse effects, oxidative stress was assessed by measuring the oxidative intrinsic potential of particles using acellular depletion DTT, Ascorbic Acid and GSH assays. Findings show a significant ultrafine fraction <100nm. Embedding in a carbonaceous matrix, Fe, Cu are the both major metal elements present in more than 94% of ultrafine fraction. Additional elements Mg, S, Ca, Cr, Zn, Ti, Al and Ba are clustered within particles, reflecting a probable remodeling of primary chemical components. An original approach by Spectroscopy Mossbauer define Iron-particles-content phases as mainly Fe⁰ (69%), and in lower proportion as Fe²⁺ (14%) and Fe³⁺ (17%). Compared to Diesel particles, brake wear exhibit high elevated oxidative potential starting with 14µg/ml of particles. Results provided pertinent information which can be used to study health effects via in vivo rodent exposure.

References:

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- 2: Gasser *et al* 2009
- 3 : Buzea *et al* 2007

Acknowledgment:

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Thematic Session: Nano: health, environment & risks

Keywords: Dispersibility, stability, TiO₂ nanoparticles, static multiple light scattering, scanning electron microscopy

Analysis of stability and dispersibility of TiO₂ nanoparticles in cell culture media by SMLS and SEM

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Abstract

Titanium dioxide (TiO₂) are among the most used nanomaterials in industries but probably the most controversial for human health. *In vitro* studies have been widely implemented to evaluate the toxicity of TiO₂ nanoparticles (NPs). However, physicochemical characterization of NPs in the biological medium prior to *in vitro* assays are not systematically performed. This is particularly critical since NPs dispersibility and stability are dependent on the TiO₂ NPs-NPs and NPs-medium interactions. Dispersibility and stability are of great importance because they yield large implications in the NPs fate and transport and dose delivered to cells. However, these parameters are commonly confused and consequently not well characterized. While stability concerns the long-term physicochemical state of NPs, dispersibility refers to the initial state of NPs immediately after the dispersion process in the medium. Even if optimal NPs dispersibility is achieved, colloidal (e.g., aggregation and agglomeration) and gravitational (e.g., sedimentation) instabilities can occur during the experiment. In this preliminary study, we perform a comprehensive characterization of the dispersibility and stability of TiO₂ NPs in cell culture media using static multiple light scattering (SMLS), scanning electron microscopy (SEM) and dynamic light scattering (DLS). The measurands obtained from SMLS, SEM and DLS are associated with these physical quantities. Three types of TiO₂ NPs dispersed in cell culture media supplemented with various BSA concentrations are studied. It is shown that same referenced TiO₂ provided by different manufacturers can have very different dispersibility and stability when dispersed with equal protocol and medium.

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Thematic Session: Nano for Imaging, diagnosis & therapy, Nanochemistry & Nanoparticles

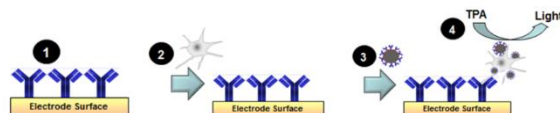
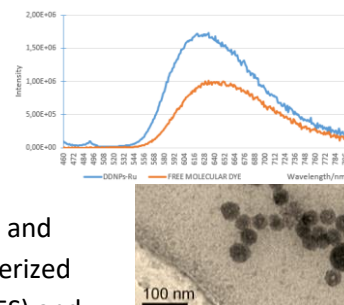
Keywords: pollutant sensing; electrochemiluminescence; ruthenium; dye doped silica nanoparticles

Detection of low amount of target pollutants in wastewater samples with dye doped, ECL-active silica nanoparticles

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The well-being of society leads to an increase of population and consequently to an increase of demand for tap water. In 2035, the estimated increase is 40% and new detection and removal systems for new pollutants (e.g. antibiotics) that are difficult to identify and remove are developed. Our goal consists in designing dye doped silica nanoparticles luminescent probes (**DDSNPs**), which could detect, the presence of pollutants before and after incineration treatment by electrochemiluminescence (**ECL**)¹ detection techniques. These luminescent sensors are made up of a silica shell which hosts luminescent Ruthenium (II) complexes. The strategy relies on the design of a series of dyes with pendant alkoxy silane function that will be hydrolyzed with a silica molecular precursor (e.g. tetraethoxysilane) yielding **DDSNPs**. Compared to the free-molecular dye in solution, suspensions of **DDSNPs** show enhanced stability and photophysical parameters. The formation of these nanoparticles will be performed by the two main synthesis pathways: normal microemulsion (path **A**) and reverse-microemulsion (path **B**). We performed both syntheses and fully characterized the obtained nano-objects from a morphological point of view (TEM, DLS, ICP-AES) and physical point of view (optical properties). The **DDSNPs** were post-functionalized with thiol pending groups to allow strong binding on a gold electrode². In suspension, the nanoparticles generate an intense ECL signal in presence of TPA as co-reactant. As illustrated, these **DDSNPs** are being used as labels within antibody sandwich assays for the highly sensitive detection of pathogenic bacteria, e.g. E. coli.



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