

11, 12 & 13 septembre

Nanomatériaux: Nanochimie, synthèse et assemblage

Nanoparticle, assembly, magnetism, collective properties

## How to enhance the magnetic properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles?

### Synthesis and assembly strategies

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Nanoparticles represent a true alternative to build high performance technological devices. At the nanoscale, the physical properties can be modulated significantly as a function of size and shape, and also by taking into account collective properties of nanoparticle arrays. In the field of nanoparticles, core-shell nanoparticles combining exchange –coupled magnetic materials with enhanced magnetic anisotropy became very attractive because they offer the possibility to circumvent one of the most striking limitations at the nanoscale: low magnetic stability against temperature resulting from size reduction. High magnetic anisotropy of nanoparticles is mandatory for further development of new rare-earth free applications such as mass storage media or sensors. We focus here on the fundamental understanding of bimagnetic nanoparticles combining a ferromagnetic Fe<sub>3-d</sub>O<sub>4</sub> core and an antiferromagnetic CoO shell which result in enhanced magnetic anisotropy with respect to Fe<sub>3</sub>O<sub>4</sub> nanoparticles. This material is discussed as matters of nanoparticles synthesis and assembling which rule intrinsic and collective properties, respectively. Advantages and limitations of these systems will be presented as well as, briefly, alternatives.

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K. Sartori *et al. under preparation*

11, 12 &amp; 13 septembre

Session nanoparticles

Keywords: 'nucleation, Turkevich synthesis, gamma and pulse radiolysis.'

## Nucleation mechanism of silver nanoparticles in the Turkevich citrate method

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Our study concerns the dynamics of nucleation in the processes of metal ion reduction, in particular the double role of the sodium citrate as the reducer and the stabilizer in the Turkevich method of nanoparticles hot synthesis. For that purpose, we used the techniques of the gamma and pulse radiolysis. We chose to study the reduction of the silver ions because they are monovalent and their reduction requires one single step. The standard potential of the initial reduction step of ions in atoms ( $E^{\circ}(\text{Ag}^+ / \text{Ag}^{\circ}) = -1.8 V_{\text{NHE}}$ ) is very negative, and should require a strong reducing agent.

According to our results on the yields and kinetics obtained using gamma and pulse radiolysis, the  $\text{Ag}^+$  reduction is not due to the first electronic transfer from the citrate. However,  $\text{Ag}_2^+$  is reduced by the second electron transfer from its oxidized radical ( $\text{Cit}(\text{H})^{\bullet}$ ). The reduction potential of the second electron transfer is thus calibrated as  $E^{\circ}(\text{CO}_2 + \text{DCA} / \text{Cit}(\text{H})^{\bullet}) < E^{\circ}(\text{Ag}_2^+ / \text{Ag}_2) = -1.2 V_{\text{NHE}}$ . The Turkevich synthesis mechanism is discussed.

11, 12 & 13 septembre

**Session:** Nanophysics and nanochemistry on surfaces

**Keywords:** scanning probe microscopy, scanning microwave microscopy, calibration, nanoscale capacitors, capacitance measurements.

## Capacitance measurements at nanoscale with scanning microwave microscopy (SMM)

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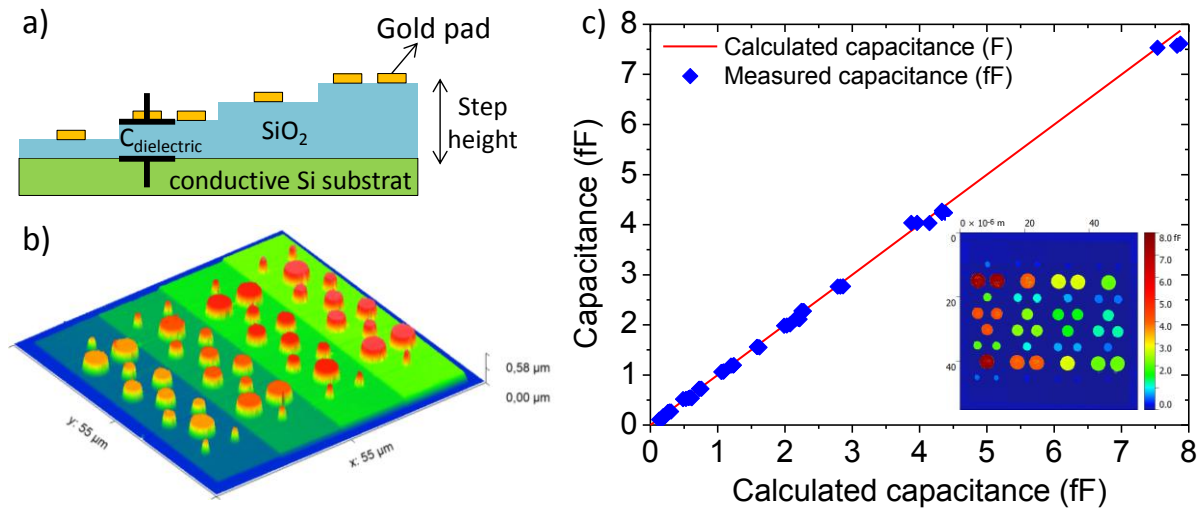
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Among various nanostructured devices, nanoscale capacitors have attracted great interest for the semiconductor industry that adopts the "3D Power scaling" method for a reduction in energy consumption. Current methods for reliable and comparable capacitance measurements at the nanoscale remain challenging. However, a non-destructive quantitative characterization tool, the SMM, has been developed to characterize nanodevices at microwave frequencies with nanometer resolution.

Briefly, the SMM consists of an AFM combined with a vector network analyser (VNA), which sent a signal (GHz range) via a transmission line to the conductive AFM tip. The tip irradiates the signal over a local region on the sample and comparing the incident and back-reflected signals, the  $S_{11}$  reflection parameter is extracted by the VNA and acquired simultaneously with the topographical image.

For quantitative measurements a fundamental step is the "calibration" of the transmission line, whose aim is to convert  $S_{11}$  into capacitance values of the sample under study.

Recently, SMM calibration procedures have been proposed [1] [2]. One of them [1] requires nanocapacitors consisted by size-controlled gold pads on silica layers. The theoretical capacitance values are calculated from the topography. The advantage of the method relies on the information obtained from  $S_{11}$  measured on 3 nanocapacitors which allows to correct the capacitance values of the others considered unknown. Here we present the results obtained when random selection (1000 draws) is made for these 3 references among 48. First results show that the corrected capacitance values for reference capacitors agree with the theoretical values within  $\pm 4\%$ .



**Figure 1.** (a) Sketch of the capacitance calibration sample. It consists of a three-layer stacked sample of doped silicon, silicon oxide, and gold pads acting as small capacitors. (b) 3D view of AFM topography of the calibration sample with SiO<sub>2</sub> step heights of 58 nm, 114 nm, 162 nm, and 209 nm. (c) Capacitances deduced from measurements vs. calculated capacitance values obtained for a draw (ranging from 0.1 fF to 8.0 fF). The bottom right inset shows the capacitance image obtained after calibration.

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11, 12 &amp; 13 septembre

Session: Nanochemistry, synthesis &amp; assembly

Keywords: 'Cycloparaphenylenes, fullerenes, DFT, molecular self-assembly, Nanocarbon'

## Interaction between two [10]CPPs and (C<sub>59</sub>N)<sub>2</sub> induced by cooperative complexation

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Just as it is possible to fill carbon nanotubes with fullerene molecules (so called 'peapods'), by analogy 1:1 complexes of fullerenes with cycloparaphenylenes (CPPs)<sup>1</sup> have been reported, highlighting a high size selectivity of the [10]CPP to the specific fullerene C<sub>60</sub>.<sup>2</sup>

The objective of the current work is two-fold, namely to explore different binding modes for CPPs owed to non-covalent aromatic interactions, and to manage charge-transfer processes within the self-assembled architecture (Figure 1). Towards these goals we expand the scope of encapsulating fullerene cages by CPPs by introducing the dumbbell-shaped bisazafullerene (C<sub>59</sub>N)<sub>2</sub> species as an N-doped fullerene analogue of C<sub>60</sub>, where a carbon atom is replaced by nitrogen.<sup>3</sup> Its extended length allows the capture of not one but two [10]CPP molecules, whose interaction can be explored via a combination of DFT calculations, NMR measurements and UV-Vis spectra.

Successfully developing the fullerene encapsulation process to include different encapsulated species and multiple CPPs opens the way to different molecular machine architectures, and provides a potential templating route to CPP polymerisation.

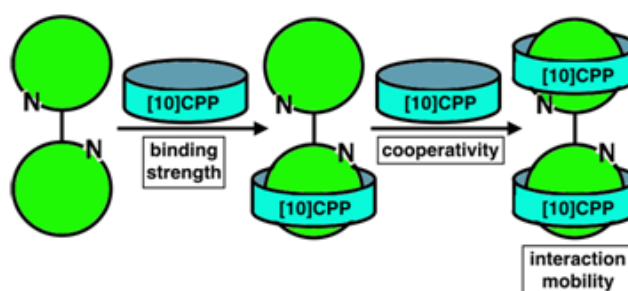


Figure 1 : The [10]CPP $\supset$ (C<sub>59</sub>N)<sub>2</sub> $\subset$ [10]CPP complex, addressing fundamental questions in supramolecular chemistry of carbon materials.

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11, 12 &amp; 13 septembre

Session Nanomatériaux : Nanochimie, synthèse et assemblage

Keywords: microwave, upconverting, cycling temperature, solvothermal, sub-3 nm

## Microwave-assisted solvothermal synthesis of inorganic nanoparticles: a promising pathway towards homogeneous sub-3 nm upconverting nanoparticles

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Lanthanide-based upconverting nanoparticles (UCNP) show the fascinating property of converting biologically benign low energy Near-Infrared (NIR) photons into high energy visible light with narrow emission bands<sup>[1]</sup>. Currently, biological applications focus on the use of sub-10 nm nano-objects promoting fast renal excretion. However, as the surface to volume ratio and surface quenching are increasing with size reduction, it is still a challenge to produce sub-10 nm hexagonal NaREF<sub>4</sub> (RE=Rare-Earth) which keep their brightness.

Typical solvothermal synthesis of such UCNPs can be decomposed into 3 main steps: at first ligand exchange from Rare-Earth precursors (chloride) to oleates, then precipitation with sodium and fluoride, and finally high temperature annealing to achieve growth and phase transition from kinetic cubic phase to thermodynamic hexagonal phase which appear sequentially<sup>[2]</sup> (hexagonal phase giving higher upconversion efficiency than the cubic one).

In this talk, the improvement of the two latter key steps with our own composition Na(Yb-Gd)F<sub>4</sub>:Tm will be highlighted:

- (1) Firstly, the influence of the mixing of sodium and fluoride<sup>[3]</sup> on the final growth will be briefly discussed.
- (2) Then, the use of microwave heating for size reduction and time shortening will be commented.

Finally microwave heating profile enhancement to cycling temperature<sup>[4]</sup> will be detailed, to reach homogeneous sub-3nm sizes.

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11, 12 &amp; 13 septembre

Session (Nanomaterials, nanophysics and nanochemistry on surfaces)

Keywords: self-assembly, on-surface synthesis, plasmonics, structure-property relationship

## Nanoplasmonic surfaces from self-assembled block copolymer thin films

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Materials with a high and tunable refractive index are attractive for nanophotonic applications. In this contribution, we propose a straightforward fabrication technique of high-refractive index surfaces based on self-assembled nanostructured block copolymer thin films. The selective and customizable metal incorporation within the poly(2vinylpyrrolidone) domains of poly(styrene)-*block*-poly(2vinylpyrrolidone) (PS-*b*-P2VP) copolymer thin films of different morphology gives access to nanoplasmonic surfaces of controlled structure. In particular, the incorporation of gold in out-of-plane PS-*b*-P2VP copolymer lamellae produces azimuthally isotropic plasmonic nanostructures of defined geometries. The nanostructures were analyzed using microscopy and small-angle X-ray scattering techniques. Variable-angle spectroscopic ellipsometry was used to relate the geometrical parameters of the metallic features and the resulting refractive index of the patterned surfaces. In particular, nanostructured gold patterns with a high degree of homogeneity and a gold content as low as 16 vol% reaches a refractive index value of more than 3 in the visible domain. Our study thus demonstrates a new route for the preparation of high refractive index surfaces with a low metal content for optical applications.

# Fluctuations in a NESS: is there a universal behavior ?

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The fluctuation-Dissipation Theorem is a cardinal tool of Statistical Physics. This relation yields to the Equipartition Principle, thanks to which we can link the fluctuations of an observable with the temperature of the system. All of this is nevertheless granted at *equilibrium*. Our purpose is to test what happens out of this safe region.

In our experiment, shown in Fig. 1, we study a system in a Non equilibrium Steady State (NESS): a silicon micro-cantilever subject to a heat flux due to a laser heating. We measure the thermal noise driven deflexion and torsion and quantify the amplitude of the fluctuations with an effective temperature  $T^{\text{eff}}$ , extending the equipartition principle:

$$\frac{1}{2}k_B T^{\text{eff}} = \frac{1}{2}k \langle x^2 \rangle$$

with  $k_B$  Boltzman's constant,  $k$  the stiffness and  $\langle x^2 \rangle$  the mean square deformation. Out of equilibrium, an *excess* of fluctuations is usually expected, as found out for example by Conti et al. in a similar system<sup>1</sup> (Fig. 1). Following Geitner et al.<sup>2</sup> we find on the contrary a strong *deficit* of thermal noise of the cantilever with respect to the average temperature  $T^{\text{avg}}$  of the system ! Further experiments and theoretical progress are thus necessary to clarify these contracticting behaviors.

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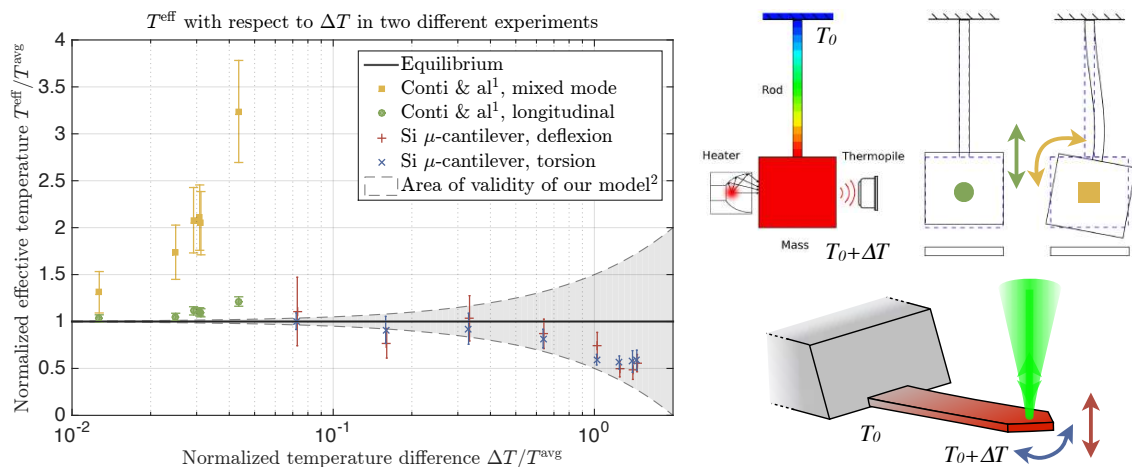


Figure 1: (Left) Effective temperature  $T^{\text{eff}}$  of a system under a heat flow as a function of the difference of temperature  $\Delta T$  at its extremities. All temperatures are normalized to the average temperature  $T^{\text{avg}}$ . (Upper right) Conti's setup<sup>1</sup>. (Lower right) Our experiment<sup>2</sup>.



11, 12 &amp; 13 decembre

Session: Nanochemistry, synthesis &amp; assembly

Keywords: 'monocrystalline nanomaterials', 'self-assembly', 'nanoscale patterns', 'epitaxial welding', 'bottom-up nanopatterning'

## Self-assembled monocrystalline patterned nanomaterials

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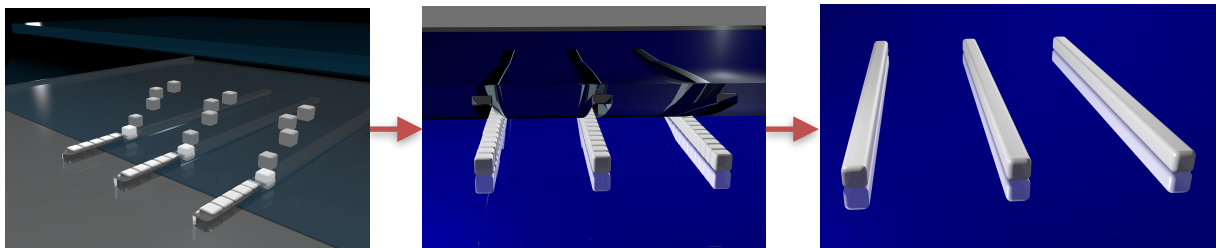
**Monocrystalline** materials are desirable for many optoelectronic applications, from solar cells to light-emitting diodes. In metals, grain boundaries cause electrons scattering, which reduces the conductivity; in semiconductors, they effectively decrease carriers lifetime and mobility, leading to non radiative recombinations, and thus reduce performance. Only few materials can be grown as monocrystalline, at the price of expensive and time consuming processes.

**Nanostructuring** has proven effective in enhancing light-matter interaction in opto-electronic devices, via optical resonances. This also has the advantage to use less material, to reduce bulk recombinations and to employ alternative geometries for the device architecture. However, by nanostructuring monocrystalline materials, much of the expensive materials is wasted in the patterning process, making this approach inefficient.

Up to date, there is no bottom-up technology available to obtain **monocrystalline materials patterned at the nanoscale**. Here, we demonstrate a new approach that meets this challenge. This is based on the *self-assembly* and *welding* of individual silver nanocube subunits, resulting in a continuous monocrystalline material.

First, we show that by capillary forces we can assemble silver nanocubes on an arbitrary nanoscale pattern, where the individual nanocubes are in a face to face configuration.

Next, we *epitaxially* weld the individual nanocube subunits at **room temperature** to produce continuous and conducting lines. We provide *HR-TEM* measurements at the interface to show the monocrystallinity of the assembled and welded cubes. We also present *electrical* and *optical measurements* to show that nanostructures obtained with this process outperform those made by thermal evaporation.



11, 12 &amp; 13 septembre

Session Nanophysics and nanochemistry on surfaces

Keywords: Aluminium Nitride, MBE, Au monolayer, NC-AFM

## Stabilization of Au Monatomic-High Islands on the $(2\times 2)$ - $N_{ad}$ Reconstructed Surface of Wurtzite AlN(0001)

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Most metals grow in the form of three-dimensional (3D) clusters at the early stages of their deposition on insulating substrates [1]. This situation generally results from the unfavourable surface and interface free energies balance involved in the formation of two-dimensional (2D) islands. Obtaining 2D metal islands on insulating substrate is thus a challenge. We succeed to obtain 2D metal islands of one mono-atomic high on the surface of the wide band gap semiconductor aluminium nitride (AlN, 6.2 eV).

RHEED spectra and low temperature NC-AFM images demonstrate that Au grows on the AlN(0001)  $(2\times 2)$ - $N_{ad}$  reconstructed surface as large (>100 nm) monolayer islands that form moiré patterns [1]. These experimental data allow us to build atomic models that are used as input for first-principles DFT calculations. These calculations show that the hexagonal Au adlayer interacts locally with the substrate via the acceptor and donor sites existing on the  $(2\times 2)$ - $N_{ad}$  reconstructed surface [2]. These interactions lead to local distortions of the hexagonal layer. Au adsorption is accompanied (i) by a global vertical charge transfer from the AlN substrate, that fulfills the electrostatic stability criterion for a polar surface, and (ii) by lateral charge transfers mediated by the reaction of Au with the acceptor and the donor sites of the polar substrate.

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11, 12 &amp; 13 septembre

Session: Advanced Characterization

Keywords: Environmental TEM, CeO<sub>2</sub> nanocubes, in situ compression, young modulus, EELS, DFT

## Mechanical behavior of cerium oxide nanocubes studied by in situ Environmental TEM compression in the elastic regime and DFT+U Simulations

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This contribution focuses on the study of the mechanical behavior of individual cerium dioxide, or ceria (CeO<sub>2</sub>), nanocubes about 20 to 50 nm in size and synthesized at ORNL, USA. In situ mechanical tests were performed in the compression mode using a Hysitron PI95 picoindenter fitted in a Cs-corrected FEI Titan Environmental Transmission Electron Microscope (ETEM installed at CLYM, Lyon) operating under vacuum or with a partial pressure of gas. With the ETEM, the oxygen vacancy content of ceria can be controlled by using an oxidizing atmosphere to compensate the departure of oxygen from the lattice during a prolonged exposure to the electron beam [1]. Electron Energy Loss Spectroscopy (EELS) was first used to calibrate the irradiation-induced substoichiometry in the range CeO<sub>2</sub> – Ce<sub>2</sub>O<sub>3</sub> (or CeO<sub>x</sub>, x decreasing from 2 to 1.5) as a function of the electron dose. Accordingly, the Young modulus was measured as a function of the substoichiometry with the help of Digital Image Correlation on the same nanocube tested under different environments (vacuum or O<sub>2</sub>).

To better characterize the effect of the reduction process (valence change Ce<sup>4+</sup> into Ce<sup>3+</sup> from cerium dioxide to the sesquioxide form) on the mechanical properties, we performed DFT+U simulations on bulk systems with various CeO<sub>x</sub> compositions. The crystallographic phases stabilized by these calculations and Young moduli are in agreement with the literature [2] and with our experimental diffraction and mechanical results.

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11, 12 &amp; 13 decembre

Session : Nanomaterials

Keywords: self-assembled monolayer; push-pull chromophore; solvent; SERS; DFT

## SERS and DFT combined study of push-pull chromophore orientation within self-assembled monolayers

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This work reports on a joint experimental/theoretical hybrid approach in order to provide information on the orientation of deposited small organic molecules within self-assembled monolayers (SAMs)<sup>1</sup> onto a gold surface. Among various  $\pi$ -conjugated molecules, we have focused our attention on the extensively studied push-pull chromophores<sup>2</sup> that have found their slot in many optoelectronic applications<sup>3</sup>. The latter are strongly dependent on the molecule orientation on the surface.

We have evidenced from an elegant Surface Enhanced Raman Spectroscopy (SERS)<sup>4</sup>/Density Functional Theory (DFT) joint study the possibility to probe the arrangement of deposited thin films of push-pull chromophores. According to this approach, we have also shown that depending on the experimental conditions, *i.e.*, the solvent nature or the coating methods, noticeable differences can be highlighted by SERS allowing to select the right conditions to tune the surface properties. In addition, by this mean it appears easy to analyse the presence or not of some defects, in terms of arrangement and/or morphology, and correlate the obtained properties to those imperfections. Based on the study we have evidenced different points: (i) the push-pull chromophores are standing perpendicularly rather than flat on the surface, (ii) the solvent impacts strongly on the structure of the chromophores promoting, in the case of dichloromethane solvent, the quinoid form, and finally (iii) drop casting favours the formation of aggregates unlike in SAMs. We are confident that the strategy is valuable and worth pursuing because this unique combination of SERS/DFT methods makes this approach very interesting and complementary among the various surface analysis techniques.

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11, 12 & 13 decembre

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11, 12 &amp; 13 septembre

Session (Nanophysics and nanochemistry on surfaces)

Keywords: polymerization, metal surface, oxidative coupling, covalent network

## On-surface Synthesis of Aligned Functional Nanoribbons Monitored by Scanning Tunnelling Microscopy and Vibrational Spectroscopy

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In the blooming field of on-surface synthesis, molecular building blocks are designed to self-assemble and covalently couple directly on a well-defined surface, thus allowing the exploration of unusual reaction pathways and the production of specific compounds in mild conditions. Up to now, most of the single-layered surface covalent organic frameworks (SCOFs) have been prepared by Ullmann dehalogenation reactions of brominated aromatic compounds or trimerization of diboronic acids. Here we present our results concerning the creation of functionalized organic nanoribbons on the Ag(110) surface by mean of an oxidative coupling unprecedented in the literature<sup>1</sup>. Interestingly, length of the resulting nanoribbons could be efficiently controlled by mean of the temperature deposition whereas the anisotropic substrate could act as an efficient template fostering the alignment of the nanoribbons, up to the full monolayer regime. <sup>[1]</sup>

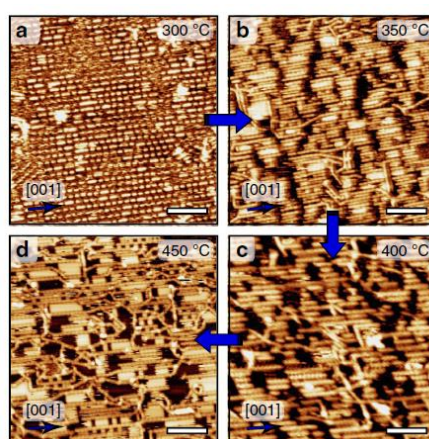


Figure 1. Nanoribbon formation and their evolution upon further annealing

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11, 12 & 13 septembre

Session: Nanobiologie -Biotechnology

Keywords: Liver, malignant tumor, Magnetic nanoparticles, simulation, Hyperthermia.

## Simulation of Magnetic Nanoparticles Hyperthermia in Liver Tumor

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The work presented here concerns the treatment of a cancerous tumor affecting the organ of the liver, this tumor was treated with magnetic nanoparticles of iron oxide ( $\text{Fe}_3\text{O}_4$ ). By applying a high frequency alternating magnetic field, a local heating of the tumor cell is obtained, hyperthermia is performed at a very high temperature, especially in the range of [42-46 °C]. The main interest of this study is to analyze the effect of nanoparticle distribution on the hyperthermia effect. Parameters such as maximum temperature, necrotic fraction rate, time to steady state were calculated numerically for different nanoparticles arrays in the tumoral cells. The conclusion is that a higher concentration of nanoparticles is more effective in the treatment of hyperthermia.

11, 12 &amp; 13 septembre

**Session** : Nanochemistry, synthesis and assembly**Keywords** : biocompatible nanogels, magnetic nanoparticles, magnetic hyperthermia/photothermia, drug delivery systems, cancer therapy

## Multiresponsive biocompatible hybrid nanogels for a controlled release of doxorubicin by magnetic hyperthermia and photothermia for a new cancer theranostic approach

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Hybrid nanogels, composed of thermoresponsive polymers and inorganic responsive nanoparticles, such as magnetic nanoparticles (MNPs) and gold nanorods (AuNRs) are highly interesting for biomedical applications. Their polymeric matrix makes them able to uptake and release high quantities of drugs, whereas nanoparticles can generate heat when exposed to an alternating magnetic field (AMF) for MNPs, and to a near-infrared light for AuNRs. This presentation focuses on the synthesis and the characterization of biocompatible, pH- and thermoresponsive nanogels, based on oligo(ethylene glycol) monomers (OEGMAs), methacrylic acid (MAA) and encapsulating MNP and/or AuRN for remotely triggered doxorubicin (DOX, anticancer drug) release, by magnetic hyperthermia or photothermia. Hybrid magnetic, plasmonic and magneto-plasmonic nanogels were synthesized. These nanogels have a hydrodynamic diameter between 200 and 500 nm and a volume phase transition temperature (VPTT) from 30° to 54°C. The nanogels swelling-deswelling behavior can be induced by several stimuli (temperature, pH, AMF, NIR-L). These results demonstrate that MagNanoGels are excellent nanocarriers for enhancing cellular internalization enhancing DOX cytotoxicity and that DOX release was significantly enhanced upon exposure to AMF in athermic conditions. In addition, PlasMagNanoGels can efficiently generate heat by photothermy for thermotherapy. Therefore, the intrinsic properties of MNPs for magnetic targeting and as contrast agents for Magnetic Resonance Imaging (MRI), make these nanogels ideal candidates for a new theranostic approach (diagnosis and treatment) against cancer.



11, 12 &amp; 13 septembre

Session Nanophysics and nanochemistry on surfaces

Keywords: Aluminium Nitride, MBE, Au monolayer, NC-AFM

## Stabilization of Au Monatomic-High Islands on the $(2\times 2)$ - $N_{ad}$ Reconstructed Surface of Wurtzite AlN(0001)

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Most metals grow in the form of three-dimensional (3D) clusters at the early stages of their deposition on insulating substrates [1]. This situation generally results from the unfavourable surface and interface free energies balance involved in the formation of two-dimensional (2D) islands. Obtaining 2D metal islands on insulating substrate is thus a challenge. We succeed to obtain 2D metal islands of one mono-atomic high on the surface of the wide band gap semiconductor aluminium nitride (AlN, 6.2 eV).

RHEED spectra and low temperature NC-AFM images demonstrate that Au grows on the AlN(0001)  $(2\times 2)$ - $N_{ad}$  reconstructed surface as large (>100 nm) monolayer islands that form moiré patterns [1]. These experimental data allow us to build atomic models that are used as input for first-principles DFT calculations. These calculations show that the hexagonal Au adlayer interacts locally with the substrate via the acceptor and donor sites existing on the  $(2\times 2)$ - $N_{ad}$  reconstructed surface [2]. These interactions lead to local distortions of the hexagonal layer. Au adsorption is accompanied (i) by a global vertical charge transfer from the AlN substrate, that fulfills the electrostatic stability criterion for a polar surface, and (ii) by lateral charge transfers mediated by the reaction of Au with the acceptor and the donor sites of the polar substrate.

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Session Nanophysics and nanochemistry on surfaces

Keywords: nano-island, charge transfer, NC-AFM, KPFM

## Controlling the electric charge of gold nanoplatelets on an insulator by field emission nc-AFM

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Flat metallic islands on an insulating substrate can be used as electrons reservoir to contact a molecule or a graphene nanoribbon in a planar geometry for molecular applications. The challenge is then to stabilize the charge on a metallic nanocrystal for a time long enough to perform in-plane operations. Here, we report on the controlled charging in UHV environment of 2D Au nanocrystals deposited on a SiO<sub>2</sub> insulating substrate. We image the platelets in the nc-AFM mode [1] and characterize their charge state by Kelvin Probe Force Microscopy (KPFM) [2,3]. Our results demonstrate that the charge can be controlled by electron field emission to or from the tip of a nc-AFM by monitoring  $\Delta f(V)$  spectroscopy curves. The procedure works for both polarities, electrons being emitted by the tip or the substrate. As shown by an analytical model and complementary numerical simulations, the rise of the island's potential upon charging leads to a constant charging current and tip-island electric field [4]. Our measurements suggest that this method can be used to set the island's potential with a single-electron precision. The procedure is robust and opens the way to original experiments, such as establishing a bias at the extremities of a molecule connected between two islands or exploring locally the charge leaking mechanisms across an insulating layer.

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11, 12 &amp; 13 décembre

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Keywords: nano, gold, catalyst, oxidation, c-c coupling

## Nanogold particles. Efficient heterogeneous catalysts for oxidation and C-C couplings reactions.

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### Abstract

Gold has long been considered to be chemically inactive and particularly without any catalytic activity. It was used mainly for coinage, jewelry, and other arts.

However, in 1987, Haruta and Hutchings published, each on his side, articles that revealed an unsuspected catalysis activity of supported gold in CO oxidation [1] and ethyne hydrochlorination reactions [2]. Very quickly, the catalytic activity of gold was related to the size of its particles. Indeed, it is now established that gold has a catalytic activity if the particle size is less than 5 nm.

This paper focuses on the different results obtained for gold as a supported metal for the catalysis of organic molecule oxidation reactions and organic molecules coupling reactions. We will particularly present the influence of different parameters (particle size, method of preparation, nature of the support, addition of a second metal, ..) on the catalytic performances (activity, selectivity, stability) in cyclohexene oxidation [3, 4] and propargylamine synthesis via a one pot three-component coupling of amines, alkynes and a methylene source [5].

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