



Livret des résumés et programme de la journée thématique du GDR Plasmonique Active





PROGRAMME DES PRESENTATIONS

9.30 - 10.00	Accueil des participant(e)s
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10.15 - 10.55	Azzedine Boudrioua Effets plasmoniques des réseaux de nanoparticules métalliques sur les propriétés des sources de lumière organiques (Université Sorbonne Paris Nord)
10.55 - 11.15	Shuwen Zeng Ultra-sensitive Plasmonic Biosensors based on Two-Dimensional NanoMaterials (UTT, Troyes)
11.15 - 11.45	Pause-café
11.45 - 12.05	Thanh Ha Duong, plasmonic nanostructure based on plant virus (Université Paris Cité)
12.05 - 12.25	Wajdi Chaâbani, Self-Assembly of Anisotropic Plasmonic Nanoparticles in Confinement (Université Paris Saclay)
12.30 - 13.45	Déjeuner (sur place)
13.45 - 14.05	Emmanuel Maisonhaute Transient Electrochemical Tip Surface-Enhanced
	Raman Spectroscopy (EC-Tip-SERS): Concept and Applications in Electrocatalysis
	and Material Science (Sorbonne Université)
14.05 - 14.25	Yun Luo , Aryl diazonium salts encoded plasmonic nanoparticles for multiplex color Raman imaging (Université Paris Cité)
14.25 - 14.45	Théo Géronimi-Jourdain, a direct visualization of photonics modes at the origin
	of lattice plasmon resonances (Université Paris Cité)
14.45 - 15.05	Elise Bailly, Quantitative modelling of photoluminescence from light-emitting metasurfaces via absorption calculations (Université PSL)
15.05-15.35	Pause-café
15.35 - 15.55	Fabien Miomandre, Smart surfaces made of gold nanoparticles functionalized by
	luminescent and redox-active molecules (Ecole Normale Supérieure Paris-Saclay)
15.55 - 16.15	Aïcha Azziz, Observation of DNA stand interaction with SERS (Le Mans
	Université)
16.15 - 16.35	Eric Brémond, Modeling the Emergence of the Plasmon Resonance in Noble Metal
	Nanoclusters (Université Paris Cité)
16.35 - 17.00	Clôture de la journée thématique 2022 : conclusions et informations



Effets plasmoniques des réseaux de nanoparticules métalliques sur les propriétés des sources de lumière organiques

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Les nanoparticules métalliques périodiques (PMN : *Periodic Metallic Nanoparticules*) permettent un contrôle précis de l'interaction entre des émetteurs et les effets plasmoniques qu'elles génèrent notamment dans le contexte des diodes électroluminescentes organiques (OLED). Les PMN présentent, à courte période (inférieure à la longueur d'onde de résonance \Box_R) une résonance plasmonique de surface localisée (LSPR), et elles donnent lieu à des résonances appelées résonances plasmoniques de réseaux (PLR) à des longueurs périodes comparable à \Box_R . Ces PLR apparaissent, en plus des LSPR, à proximité des anomalies de Rayleigh du réseau. En outres, ce type de structures PMN présente un grand intérêt pour améliorer l'émission des émetteurs organiques, leur directivité et cohérence. Ces effets peuvent avoir un impact positif sur l'efficacité des OLED.

Dans ce travail, seront présentés et discutés les effets plasmoniques des réseaux métalliques périodiques sur les propriétés d'émission des émetteurs organiques. Entre autres, nos travaux mettent en évidence le rôle crucial des anomalies de Rayleigh, qui peuvent être considérées comme l'intermédiaire entre les réponses plasmoniques individuelles et photoniques collectives. Les résultats obtenus indiquent que le réglage des paramètres géométriques du réseau offre la possibilité de sélectionner un processus de couplage particulier d'un effet localisé à une réponse en champ lointain, et selon la nature du couplage l'émission peut être fortement modifiée en augmentant la densité d'états ou en fournissant des ordres diffractifs.



Ultra-sensitive Plasmonic Biosensors based on Two-Dimensional NanoMaterials

Shuwen ZENG, Université de Technologie de Troyes

Abstract: Surface plasmon resonance sensors are commonly used an effective tool for real-time monitoring biomolecular interactions. The sensing mechanism is based on the evanescent field perturbation at the metallic sensing substrate induced by the binding of chemical and biological molecules. Molecular binding interactions could be measured from the signal of reflected light, under the condition that the surface plasmon resonance is excited by the incident light. In this talk, I will present the use of hybrid 2D nanomaterials-based metasurface nanostructure as an enhanced sensing substrate. The thickness of the plasmonic sensing substrate is tuned in an atomic scale and optimized to improve the sensing capability. Here, both a sharp phase signal change and phase-related Goos-Hänchen signal shift were achieved due to the strong resonance at the surface of the sensing film. The enhanced plasmonic sensitivities of 2D nanostructures were systematically investigated. It is worth noting that the tunability of atomic layer led to the sensing substrate optimized with a narrow scale < 1 nm. Through a precise engineering of the metasurface substrates, 3 orders of magnitude improvement of the sensitivity were demonstrated compared to the one with pure gold sensing substrate. This hybrid 2D nanomaterial-based metasurfaces would provide a good opportunity for developing portable theranostic devices in clinical applications.



PLASMONIC NANOSTRUCTURE BASED ON PLANT VIRUS

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The ability to construct three dimensional architectures via nanoscale engineering is important for emerging applications of nanotechnology in sensors, catalysis, controlled drug delivery, microelectronics, and medical diagnostics. Because of their well-defined and highly organized symmetric structures, high robustness over wide ranges of temperature, pH, buffer, and in the presence of organic solvents, viral capsid proteins then provide a 3D scaffold for the precise placement of plasmon materials yielding hierarchical hybrid materials. In this study, we use several plant viruses with different shapes and morphologies: Turnip yellow mosaic virus (TYMV), Rice yellow mottle virus (RYMV), Tobacco mosaic virus (TMV) and Potato virus X (PVX). Two ways are possible to obtain nanostructure onto capsid: grafting pre-formed nanoparticles or biomineralization.

In the first part of this work, I will present the synthesis and characterization of new nano-bio-hybrid materials, which are soluble and stable in solution. Gold nanoparticles (AuNP) of different sizes (5, 10 and 20 nm) were grafted on icosahedral capsid, according to two strategies. After purification, the resulting nano-bio-hybrids were characterized by different technics (DLS, TEM, XPS...). Then, I will present some preliminary results of these new materials in two fields of application: SERS in solution and hyperthermia.

In the second part, gold biomineralization experiments on TMV and PVX will be described. The size, morphology, monodispersity of AuNP and gold assembly on virus were studied according to the experimental conditions (concentrations of reactant, number of cycle, nature of reductant...) and in situ TEM observations directly in liquid media were also performed to unravel the nucleation and growth mechanisms.





Self-Assembly of Anisotropic Plasmonic Nanoparticles in Confinement

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Three-dimensional (3D) supercrystals (SCs) of plasmonic nanoparticles are a novel class of materials with exciting applications in technologies such as light harvesting or metamaterials. However, their realization relies on extraordinarily regular colloidal building blocks and accurate self-assembly methods. We present here the 3D assemblies in confinement anisotropic gold nanoparticles (e.g. bipyramids) in different mold shapes prepared by soft-lithography [1]. Then, the SCs are characterized by small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM), and optical microscopy.

We demonstrate here that the polygonal mold edge directs the orientation and number domains in the SCs. In addition, by combined SAXS and SEM analysis, we have concluded that the number of domains (n) is correlated with the mold edge number (k). We conclude that n=k/2when k is pair and n=2k when k is odd. For instance, in Figure 1, we show a triangular SCs shape (k=3) presenting three domains and six Bragg spots (n=6).



Figure 1: Self-assembly of bipyramids NPs in triangular mold. (left) TEM image, (middle) SEM images of NPs assemblies in triangular mold (top and side views), (right) 2D- SAXS image and azimuthal integration

[1] C. Hamon et al. ACS Nano 8 (2014) 10694-10703



Transient Electrochemical Tip Surface-Enhanced Raman Spectroscopy (EC-Tip-SERS) : Concept and Applications in Electrocatalysis and Material Science

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The development of electrochemical techniques combined to Raman spectroscopy such as electrochemical Tip- or Surface- Enhanced Raman spectroscopy (EC-TERS or EC-SERS) have attracted considerable attention over the past years by the scientific community. This spectro-electrochemical combination provides an accurate view over electrochemical processes occurring at an electrode by acquiring simultaneously local topography, and vibrational fingerprints about the material or molecules under potential control.^[1] Based on the use of an insulated TERS tip, we introduced recently a new approach that we called EC-Tip-SERS (Figure 1). Here, electroactive molecules are adsorbed directly onto the tip that acts both as working microelectrode and single hotspot for SERS.^[3] Although the spatial resolution is lost in this configuration, interesting transient mechanistic information can be obtained. In this communication, we will present first the use of this technique on a redox- and Raman- active model molecule, the Nile blue, in which a temporal resolution in the order of millisecond can be easily attained. Then, we will consider the use of Tip-SERS in probing molecular motion within rotaxane-based giant assemblies containing porphyrins derivatives. Finally, we will demonstrate the use of transient EC-Tip-SERS in scrutinizing electrocatalytic transient mechanisms, such as those associated to the oxygen reduction reaction towards hydrogen peroxide in water using viologen SAMs as electrocatalyts.



Transient electrochemical tip-SERS setup

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- [1] Ding, S. Y., Yi, J., Li, J. F., Ren, B., Wu, D. Y., Panneerselvam, R., & Tian, Z. Q. Nature Reviews Materials, 1, (2016) 1-16.
- [2] Touzalin, T., Joiret, S., Maisonhaute, E., & Lucas, I. T. Analytical chemistry, 89 (2017) 8974-8980.



Aryl diazonium salts encoded plasmonic nanoparticles for multiplex color Raman imaging

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Bioimaging refers to the use of imaging modalities to visualize biological process and activity in a specific period. Nowadays, bio-imaging based on fluorescent dye staining has been widely applied for biological research. However, fluorescent probes (e.g. organic dyes) suffer from the spectral overlap due to their broad spectral feature and instability caused by photo-bleaching. In order to overcome these drawbacks, bioimaging based on surface enhanced Raman spectroscopy (SERS) has attracted more and more interests because of its improved imaging accuracy for following reasons: i) SERS provides multiple sets of narrow peak, resulting in low spectral overlap; ii) SERS reporters, adsorbed on nanostructured metal surface, rarely show degradation under light excitation; iii) SERS is able to generate a nanoscaled image resolution with respect to conventional fluorescence microscopy. In our work, we have explored aryl diazonium salts encoded gold and silver nanoparticles (AuNPs and AgNPs) as contrast agent for Raman imaging. Compared with the counterpart based on thiol-grafted AuNPs, aryl diazonium salts grafting leads to more stable nanocomposite because of the formed robust covalent metal-C bonding in the interface. In addition, the reaction of aryl diazonium salts usually form multilayers which can be post-functionalized. Our strategy is to prepare multilayer functionalized plasmonic NPs, as shown in Fig. 1. Three aryl diazonium salt, 4-ethynylbenzenediazonium (D-CCH), 4-cyano-benzenediazonium (D-CN) and 4-nitrobenzenediazonium (D-NO2) tetrafluoroborate, are used for grafting, playing the role of SERS tag for imaging. The obtained nanocomposite has been incubated with tumor cells, as a proof of concept for multicolor bioimaging. We further explored the application of these NPs as anti-counterfeiting taggants to secure hand-writing and inkjet printed marks.



Fig. 1. Aryl diazonium functionalized NPs for SERS bioimaging and anti-counterfeiting.



A visualization in real space of photonics modes at the origin of lattice plasmon resonances.

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Plasmonic nanostructures arranged in regular arrays support lattice plasmon modes, thought the diffraction of photonic modes of distinct orders in the plan of the substrate. These lattice modes are characterized by a reduced linewidth of the resonance and an important improvement in its quality factor, and thus can provide improved platforms in the context of non-linear optics, molecular sensing, plasmon-based lasers, or surface enhanced spectroscopies [1].

In this work, we show that the plasmon-mediated grafting of aryl films, derived from diazonium salts [2], makes it possible to map the photonic modes propagating on the surface of regular arrays of gold disks displaying surface lattice (figure below). This mapping allows us to directly identify the order of the photonic modes, which is of crucial importance for the understanding of the origin of the long-range coupling of the plasmonic structures. In addition, such grating effects, taking advantage of the diffraction of distinct orders, allows us to further investigate plasmon-mediated patterning, and opens up the route to multiplexing polymers grafting on large surface areas.



Figure (a): AFM image of a square array of gold disks (diameter 150 nm, height 50 nm, on an ITO layer), for a grating constant of 680 nm, corresponding to the diffraction of a photonic mode of (1,1) order; (b): corresponding mapping of the intensity of the electric field, obtained by the FDTD method.

References:

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Quantitative modelling of photoluminescence from light-emitting metasurfaces via absorption calculations

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Light-emitting metasurfaces are devices consisting of a nanostructured surface covered with dense ensemble of emitters. The interaction between emitters and the metasurface enables for a precise control of the emission properties. In the standard model, the emitters are considered as a collection of electric dipoles randomly oriented inside the structure, whose contribution can be added incoherently. Their emission spectrum is a Stokes-shifted counterpart of their absorption spectrum. The emission spectrum of the whole structure results from the modification of the fluorophore photoluminescence via radiative decay rate enhancement and extraction efficiency of the device. This approach does not account for modifications of the spectrum influenced by temperature and pumping conditions and cannot predict the intensity of the emitted signal. In this presentation, we present a procedure to model emission by lightemitting metasurfaces using a generalized Kirchhoff's law formalism [1]. We show that photoluminescence from metasurfaces can be modelled as the product of a local absorptivity rate by a Planckian exponential contribution depending on the temperature and the photon chemical potential. Far from material resonances, the absorptivity is extremely low. However, light emission can still occur provided that the Planckian factor takes significant values. Therefore, a quantitative and reliable modelling of emission also require accurate permittivity models in the low energy tail of the absorption spectrum. We show that Brendel-Bormann models of permittivity overcome limitations faced when using Lorentzian models. We apply our procedure to quantitatively predict the photoluminescence features of complex systems consisting of ensembles J-aggregated dyes (TDBC) deposited on metallic subtrates. [2]

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Smart surfaces made of gold nanoparticles functionalized by luminescent and redox-active molecules.

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Plasmonic surfaces made of gold nanoparticles coated on ITO have been functionalized by luminescent and redox active molecules. The aim of this study is to design smart surfaces that can be activated by a light stimulus and lead to an output signal, namely the emission of the molecule, that is strongly dependent on multiple factors among which the redox state of the molecule and surface plasmon excitation. Information coding systems can be envisioned according to this principle.

The grafted molecules are made of tetrazine derivatives, which are both redox active and luminescent. The functional surfaces have been characterized by microscopy, XPS, cyclic voltammetry and time-resolved photoluminescence. The dependence of the luminescence properties with the gold nanoparticle size, surface density and grafting method (immersion or electrodeposition) has been analyzed and the results will be discussed in this communication.



Reference :

Oliveira de MIRANDA, Livio; MAILLOT, Baptiste; BOSMI, Margarita; GALMICHE, Laurent; AUDIBERT, Jean-Frédéric; Brasiliense, Vitor; Berthelier, Lea; Bonnamour, Isabelle; Darbost, Ulrich; Miomandre, Fabien, "Synthesis and Grafting of New Luminescent and Redox-Active Tetrazine Derivatives on Gold Nanoparticles", J. Phys. Chem. C under revision.



Observation of DNA stand interaction with SERS

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Surface-enhanced Raman spectroscopy has demonstrated its ability as powerful tool that can provide us information about the structure and the conformation of molecules such as DNA. In this work, we used an Hamamatsu commercial SERS substrate [1], to study the interaction between a DNA sequence consisting of 20 Bases of poly-Thymin (PolyT) with its complementary poly-Adenin (PolyA). The PolyA strand is grafted at the surface of the gold nanostructured surface using a thiol group at the 5' extremity of the DNA strand. the SERS substrate is incubated in 450 µl of PolyA (10-4 M) in TE buffer for 15 hours. The surface is then washed to remove the PolyA excess. We assume that we form a monolayer of PolyA. Some solutions of PolyT with different concentrations (10-7, 10-6, 10-5 and 10-4 M) are successively deposited on the SERS substrate. We performed Raman mapping on the surface and we recorded 400 spectra using a 633 nm excitation wavelength. One can observe the 735 cm-1 band assigned to the ring breathing mode of the PolyA and some variations of its intensity depending on the position on the map. By changing the concentration, we observe a decrease of the average SERS intensity of this band as well as a decrease of the standard deviation of the intensity of this band. We interpret this intensity change by some modification of the orientation and flexibility of the PolyA DNA strands interacting with the PolyT [2]. The increase of the concentration of Poly-T induced a loss of flexibility of the PolyT/PolyA molecular complex. This study provides a new approach for the reliable quantification and structural analysis of biological molecules. This work was supported by the European project DeDNAed (H2020-FETOPEN2018- 2020, n° 964248).

References

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Modeling the Emergence of the Plasmon Resonance in Noble Metal Nanoclusters

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Modeling the emergence of the plasmon resonance in noble metal nanoclusters is still a challenge to tackle for theoretical chemistry. The systems are indeed too small to neglect quantum-size effects but too large to be easily assessed with quantum mechanics. In short, we present here a novel methodology based on density-functional theory (DFT) allowing for the computation and interpretation of the plasmon resonance in noble metal nanoclusters.



POSTER

Probing the dynamics at the water/hydrophobic interface through real-time SERS detection

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The nature of the interface between water and hydrophobic species has been the subject of extensive debate. However, the ubiquity of this interface in nature points towards its great significance when considering complex biomolecules and the various related chemical reactions. Current techniques and models are proven to be inadequate in providing an overall description of said interface. Thus, this study aims to (1) suggest a novel approach to understanding the dynamics of the water/hydrophobic interface utilizing surface-enhanced Raman scattering (SERS), (2) take advantage of this antagonistic interface to induce a new kind of surfactant-free silver nanostructure with high-density and stable hotspots, and (3) utilize aforementioned silver films as SERS substrates for single-molecule detection at the interface (with particular interests in biochemistry and biology).



SEM of single-layer AgNPs film on glass substrate (top) and time-resolved SERS (bottom)

All our silver films were synthesized without surfactants. These films were found to be composed of highly-monodispersed AgNPs (e.g. ~18 nm as shown on SEM). Furthermore, strong activity was observed under a 1 μ m area with a 10 μ W laser power and a 50 ms acquisition time. From this, we can say that the film made has the potential to produce surfactant-free, sensitive SERS substrates that can greatly improve future SERS analyses. These observed properties are borne out of the behavior of our manipulation of the antagonistic interface during synthesis.



POSTER

Following atomic migration and charge transfer induced by molecular adsorption on plasmonic nanoparticles

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Understanding molecular interactions with nanoparticles (NP) exhibiting a localized surface plasmon resonance (LSPR) is of great relevance for photo-catalyze chemical reactions or enhance charge transfer in optoelectronic devices. NP properties can be modified by adjusting their size, composition or by anchoring molecules at their surface. However, probing these objects down a single molecule or NP NP is an important challenge due to large size/shape dispersion, instrumental sensitivity or surrounding environment. In order to overcome these limitations, we elaborated dense arrays of plasmonic bimetallic core-shell NP by physical vapor deposition in ultra-high vacuum, on an Al₂O₃ bilayer on Ni₃Al(111) [1]. The impact of molecular adsorption on NP structure [2], molecular optical response and plasmonic properties are investigated [3]. For that, we combined STM microscopy to reveal surface topography, optical reflectance spectroscopy to follow LSPR changes, supported by finite element analysis and nonlinear vibrational spectroscopy to probe adsorbed molecules (sites, orientation and dynamics).

We present two hybrid systems where electronic/optical couplings of molecules with LSPR are revealed: 1. Carbon monoxide on Pd-Au NP on which the plasmonic response is controlled by the reversible

- migration of Pd from the core to the shell induced by CO adsorption and NP temperature (Fig. 1a). 2. Fullerene on Pd-Ag NP on which we monitor with a sensitivity of one molecule per NP, how the
- 2. Public on Pul-Ag for on which we monitor with a sensitivity of one molecule per for, now the LPRS and molecular electronic structure are modified during adsorption, evidencing charge transfer and dielectric constant change in the first vicinity of the plasmonic NP (Fig. 1b).



Figure 1: UV/Vis reflectivity change showing: (a) the impact of Pd migration at the Au shell surface on NP LSPR and (b) charge transfer from NP to C_{60} and LSPR changes.

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