

## JOURNEES PLENIERES

**2 et 3 Octobre 2024**  
**PARIS**



**Site Paris Rive Gauche**  
**Amphithéâtre Buffon**  
**15 Rue Hélène Brion, 75013 Paris**

**Chères collègues, chers collègues,**

Nous avons le grand plaisir de vous accueillir aux journées plénières du GDR Plasmonique Active (CNRS, GDR 2090) qui se tiendront à l'Université Paris Cité les 2 et 3 octobre 2024.

Au nom du bureau du GDR, je tiens à exprimer notre sincère gratitude à l'Université Paris Cité pour son accueil chaleureux, ainsi qu'à l'entreprise WITEC et au CNRS pour leur soutien financier, indispensable à la réalisation de cet événement.

Avec près de 80 participant(e)s, ces journées seront une précieuse occasion de réunir notre communauté, une dernière fois avant la fin de ce mandat, et peut-être à l'aube d'un nouveau quinquennat. Au-delà des conférences orales, nous espérons que ces deux jours favoriseront des discussions informelles enrichissantes et renforceront les liens scientifiques au sein de notre communauté.

Le tout, bien sûr, accompagné d'un *cocktail à la Parisienne* convivial pour clore ces journées dans la meilleure des ambiances.

Nous vous souhaitons d'excellentes journées plénières.

Bien cordialement,

**Au nom du bureau du GDR Plasmonique Active,**

M. Nordin FELIDJ, directeur du GDR

M. Marc Lamy de la Chapelle, directeur adjoint du GDR



## **Programme Journées plénières GDR *Plasmonique Active* (CNRS 2090)**

**Les 2 et 3 Octobre 2024  
Université Paris Cité (amphithéâtre Buffon)**

### **Mercredi 2 octobre 2024**

9h00-9h15 : Introduction (Nordin FELIDJ, Marc LAMY De La CHAPELLE)

#### Session 1:

- 9h15-9h50 : Aloyse DEGIRON (invité), laboratoire MPQ, CNRS, UP Cité, Paris.
- 9h50-10h10: Valentina KRACHMALNICOFF, ESCPI, CNRS, ESPCI, Paris.
- 10h10-10h30: Jean-Christophe VALMALETTE, IM2NP, CNRS, Université de Toulon, La Garde.

10h30-11h10 : Pause -café

#### Session 2

- 11h10-11h45 : Clémentine SYMONDS (invitée), ILM, CNRS, Université Claude Bernard Lyon 1, Lyon.
- 11h45-12h05: Jean François BRYCHE, LN2, CNRS, Sherbrooke, Canada.
- 12h05-12h25 : Julien SIMONNEAU, Nantes Université, CNRS, CEISAM, Nantes.

12h30-13h45 : Déjeuner (buffet)

#### Session 3

- 13h45-14h20: Olivier PLUCHERY (invité), INSP, CNRS, Sorbonne Université, Paris.
- 14h20-14h40: Mathias DOLCI, Institute for Complex Molecular Systems (ICMS), Eindhoven, Pays-Bas.
- 14h40-15h00: Abdelhak DHIBI, Université Paris 13, Sorbonne Paris Cité, Bobigny.

15h00-15h30 : Pause-café

#### Session 4

- 15h30-16h05 François LAGUGNE-LABARTHET (invité), Western University, London, Canada.
- 16h00-16h20: Alexandre BOUHELIER, Laboratoire Interdisciplinaire Carnot de Bourgogne, CNRS, Université de Bourgogne, Dijon.
- 16h20-16h40: Mathieu, MIVELLE, Sorbonne Université, CNRS, Institut des NanoSciences de Paris, France.

16h40-19h00: Session poster - cocktail

## Jeudi 3 octobre 2024

### Session 5

- 9h15-9h50 : Souhir BOUJDAY (invitée), Laboratoire de Réactivité de Surface, CNRS, Sorbonne Université, Paris.
- 9h50-10h10 : B. DEMIRDJIAN, Aix Marseille Université, CINaM, CNRS, Marseille.
- 10h10-10h30 Coline BELTRAMI, Laboratoire Nanotechnologie et Nanosystèmes, Sherbrooke, Canada.

10h30-11h00 : Pause-café

### Session 6

- 11h00-11h35: Ludovic DOUILLARD (invité), CEA, CNRS, Univ. Paris Saclay.
- 11h35-11h55: Eric LE MOAL, Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay .
- 11h55-12h15: Théo MINCHELLA, L2n, UTT, Troyes.

12h15-13h45 : Déjeuner - Buffet

### Session 7

- 13h45-14h20: Emmanuelle LACAZE (invitée), INSP, Sorbonne Université, Paris.
- 14h20-14h40: Samantha ROQUE, (IM2NP), UMR CNRS 7334, Université de Toulon, La Garde.
- 14h40-15h00: Charlène BRISSAUD, laboratoire ITODYS, UP Cité, Paris.

15h00-15h30 : Pause-café

### Session 8

- 15h30-16h05 Davy GERARD (invité), L2n, CNRS, UTT, Troyes.
- 16h05-16h25 Anne-Laure BAUDRION, L2n, CNRS, UTT, Troyes.
- 16h25-16h45 : Mathieu EDELY, IMMM - UMR CNRS, Université du Mans, Le Mans, France

16h45-17h30 : Table ronde : perspectives dans le domaine de la plasmonique active, renouvellement du GDR, problématiques autour du développement durable.

17h30-17h45 : Conclusion des journées plénières.

**Oraux invités**

# Why ensembles of mutually-coupled emitters are so different from individual emitters when it comes to tailor their properties with plasmonics

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Plasmonic antennas and metasurfaces have long been used to enhance and tailor the spontaneous emission of quantum emitters [1]. The design rules that have been established over the years are based on the assumption that such metallic structures operate through the Purcell effect [1]. Here, I will experimentally show that this paradigm fails for ensembles of interacting emitters and that their properties are governed by a different mechanism—the local Kirchhoff law introduced by Greffet et al. [2]. Among the manifestations of this regime, two unintuitive signatures stand out:

- 1) The emitters are not quenched by the metal, even if the latter is very lossy. In fact, radiative decay is maximized when the emitters are touching the metal [3,4].
- 2) The lifetime of interacting emitters is essentially independent of their photonic environment, even if the latter contains highly resonant features or, to the contrary, no resonance at all [5].

I will rationalize these observations with carrier thermalization arguments [5,6], discuss their fundamental implications and show how these effects can be leveraged in innovative optoelectronic devices [7].

## Acknowledgements

I acknowledge support from the European Research Council grant (ref: 771688).

## References

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- [2] J.-J. Greffet et al. *Phys. Rev. X* 8, 021008 (2018)
- [3] H. Wang, Q. Le-Van, A. Aassime, X. Le Roux, F. Charra, N. Chauvin and A. Degiron, *Adv. Opt. Mat.* 6, 170058 (2018)
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- [6] A. Caillas, S. Suffit, P. Filloux, E. Lhuillier and A. Degiron, *J. Phys. Chem. Lett.* 12, 5123–5131 (2021)
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# Extended hybridization and energy transfer in multimaterial polaritonic metasurfaces

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The phenomenon of strong coupling, which occurs when light-matter interaction prevails over damping, leads to remarkable changes in the optical properties of matter, modifying both the spectrum and the dynamics of excitations. When a large number of emitters are involved, coherent coupling of the emitters across the electromagnetic mode occurs. In metal/organic systems, the strongly coupled state (polariton) between the molecules and a propagating plasmon has an extension ranging from a few microns to several tens of microns.

We will first show how this extended coherence of organic systems strongly coupled to plasmons can be used to hybridize two different organic materials through the plasmon coupling, and mix the functionalities of different organics.

We will then present a new type of metasurface, which builds on the extended coherent states associated to plasmon/exciton polaritons. For this purpose, periodic stripes of organic dye are deposited on a continuous silver film. With a structuration exceeding the polaritonic wavelength by more than one order of magnitude, we demonstrate anisotropy generation in transition energies and emission patterns. These findings pave the way towards a novel type of artificial materials which require micro- instead of nano-structuration.

Finally, we will show how these polaritonic metasurfaces can be applied to large scale energy transfer in multimaterial arrays. To achieve this, two arrays of interlocked dyes, one donor and one acceptor, are deposited on a silver surface by successive micro-contact printing. We will demonstrate that the mixing in these polaritonic metasurfaces allows an energy transfer mechanism in strong coupling.



# Tuning the Properties of Transition Metal Dichalcogenide Flakes with Diazonium Salts

***François Lagugné-Labarthe<sup>(1)</sup>, Cédric Lambin<sup>(1)</sup>, Claire Mangeney<sup>(2)</sup>,  
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In 2D materials with semiconductor character such as transition metal dichalcogenides (TMDCs), the band gap between the valence and the conducting bands can be tuned and controlled by surface functionalization. The possibility to impart a variety of functional groups at the surface is of interest because it facilitates the tuning of the properties of an hybrid TMD flake thus opening the development of optimized building blocks for sensing, catalytical or photovoltaic applications.

Herein, we report on molybdenum disulfide (MoS<sub>2</sub>) and tungsten disulfide (WS<sub>2</sub>) single and few-layer flakes grown by chemical vapor deposition, that exhibit a photoluminescence altered in intensity and shifted to different energies upon surface chemical functionalization.<sup>1</sup> Aryl diazonium salts were selected to alter the surface properties of the TMDCs due to their spontaneous, fast, and effective reaction. We find that the reaction generates a covalent binding between TMDCs and diazonium salts. The surface functionalization proceeds in soft conditions. This modification is effective for tuning the band gap and induces a p-doping effect in MoS<sub>2</sub> with varying intensities depending on the functional group present on the diazonium salts. We show how the N<sub>2</sub> group of the diazonium salt is critical for the yield of the surface reaction compared to other small organic molecules. The topology and mechanical properties were studied by AFM while Tip-Enhanced Raman spectroscopy and Tip-Enhanced photoluminescence enabled to evaluate the spatial homogeneity of the functionalization over single flakes. Kelvin Force microscopy provided quantitative information on how the workfunction is affected by the surface functionalization.<sup>2</sup>

## References

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- [2] J. Jelken, M. O. Avilés, F. Lagugné-Labarthe, "The Hidden Flower in WS<sub>2</sub> Flakes: A Combined Nano-Mechanical and Tip-Enhanced Raman Exploration", *ACS Nano*, 2022, 16, 12352-12363

# Tailoring plasmonic nanomaterials *via* surface chemistry for biosensing and nanomedicine

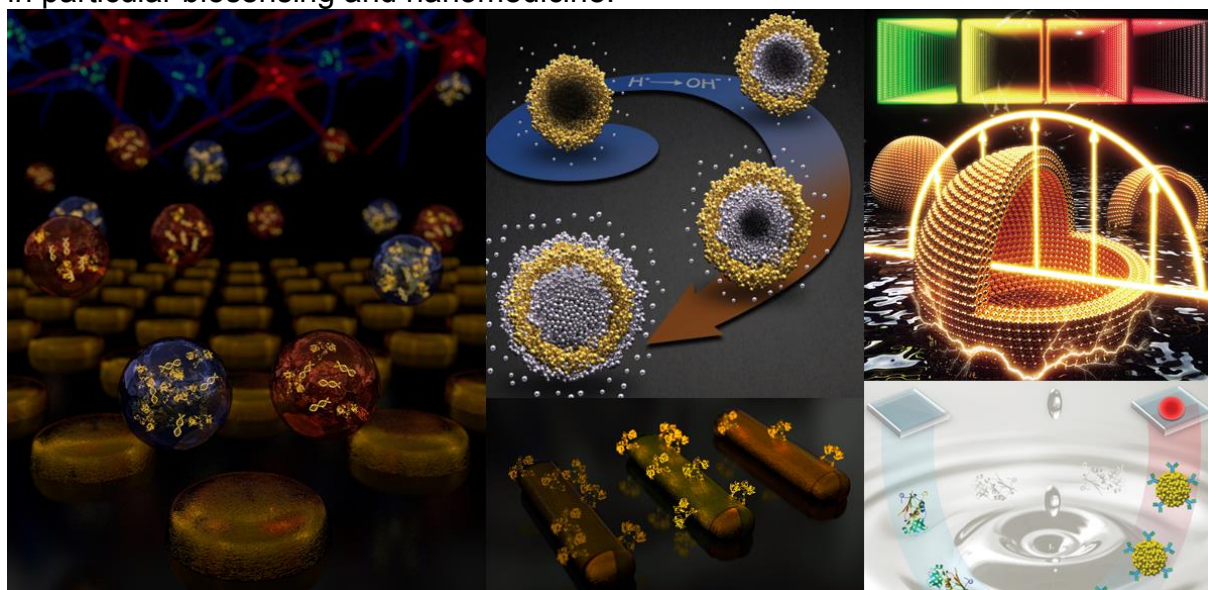
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The surfaces of materials and nanomaterials are the place of their reactivity and govern their interactions with the surrounding environment. Whether they are flat surfaces or plasmonic nanostructures, these (nano)materials are at the very core of diverse applications such as diagnosis, sensing, drug delivery and antifouling.

The input of surface chemistry to the ultimate success of these (nano)materials is undeniable, since it enables them to be shaped, stabilized and functionalized with precision and rigor, and eventually to be combined, in a controlled manner, with biological molecules. Using examples developed in our group, NanoBioSurf at Sorbonne University, methods for functionalizing and decorating these (nano)materials will be discussed, with a focus on tailoring them to the desired biological application, in particular biosensing and nanomedicine.



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# Nanoparticules plasmoniques pour l'exploration de l'interaction lumière – matière en régime de champ fort

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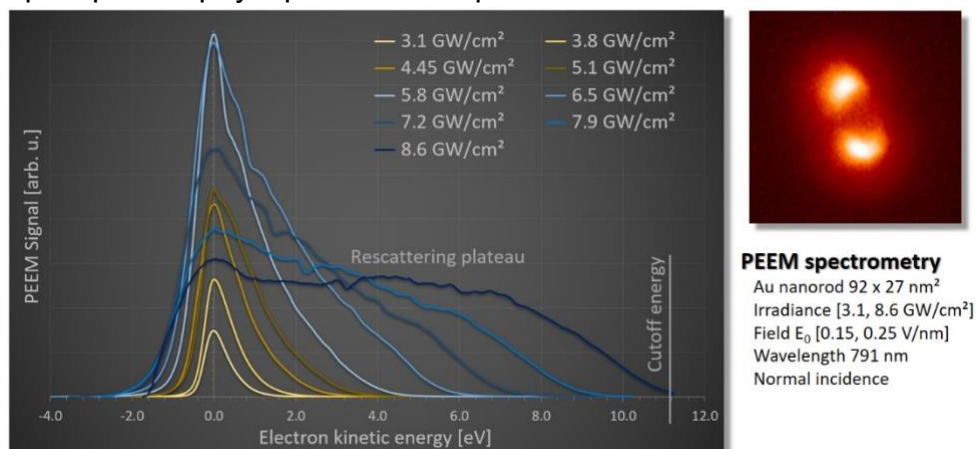
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À petite échelle, l'interaction de la lumière avec un objet métallique conduit à l'occurrence de résonances remarquables dans le spectre d'absorption, les résonances plasmons. Ces modes correspondent à des oscillations collectives cohérentes des porteurs de charge et génèrent des champs localisés de grande amplitude. La plasmonique offre ainsi la possibilité d'explorer de nouvelles propriétés physiques dans des régimes extrêmes, en particulier la physique des champs forts.

Ce travail rapporte l'emploi de nanoparticules plasmoniques comme supports d'étude de différents régimes d'émission électronique. Le mécanisme d'émission peut être continument ajusté d'une émission photoélectrique non linéaire caractéristique d'un régime de champ faible à une émission froide de type tunnel en régime de champ fort. L'étude est conduite au niveau de l'objet individuel via le suivi de la distribution en énergie cinétique des électrons émis à résonance [Dombi 2013]. En régime champ fort, les électrons voient leurs distributions d'énergie s'élargir conséquemment par effet pondéromoteur à concurrence d'une énergie de coupure. Une énergie de coupure de 10 eV est aisément obtenue pour une irradiance modeste de l'ordre de 1 - 10 GW/cm<sup>2</sup> dans la gamme infra-rouge. La figure montre l'évolution des courbes de distribution d'énergie des électrons émis par un nanobâtonnet Au individuel excité à résonance plasmonique longitudinale pour différentes irradiances. L'importance des particules plasmoniques pour la physique des champs forts sera discutée.



## References

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# Organization and plasmonic properties of gold nanoparticles controlled by liquid crystal matrices

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Using thin liquid crystal smectic films, distorted by the different molecular geometry imposed by the liquid crystal/air interface and the substrate, we create arrays of topological defects for thicknesses smaller than 300 nm [1]. The defects are strictly oriented along one single orientation defined by the substrate. When a nanoparticle is localized in the core of the defects, the disordered liquid crystal molecules of the core are locally expelled, which stabilizes the composite. Liquid crystal defects can therefore be seen as molds capable of creating nanoparticle assemblies shaped by the defect geometry [2, 3].

In this talk, I will describe our recent progresses that allow us to better understand the interactions between nanoparticles and the defects, both for nanospheres and for nanorods. The possible nanoparticle organizations that can be achieved will thus be presented together with the related plasmonic properties. I will show in particular that we can now study original optical properties of nanoparticle assemblies, in particular of oriented gold nanorod assemblies, still difficult to form without the help of these topological defects.

## References

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- [3] H. Jeridi et al., Soft Matter 18, 4792 (2022)

# Self-strong coupling in aluminum nanoantennas

J. Martin,<sup>1</sup> T. Simon,<sup>1</sup> G. Arditì,<sup>2</sup> O. Avalos-Ovando,<sup>3</sup> F. Lamaze,<sup>1</sup> J. Proust,<sup>1</sup> A. Govorov,<sup>3</sup> M. Kociak,<sup>2</sup> O. Stefan,<sup>2</sup> and D. Gérard<sup>1</sup>

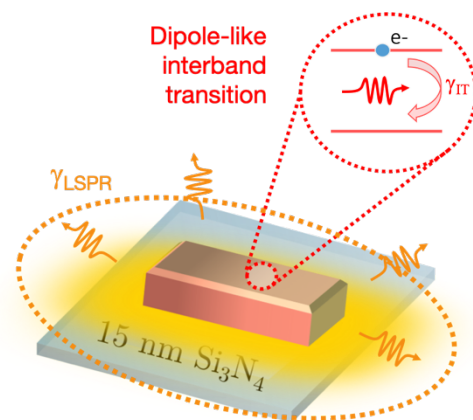
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In the strong coupling regime, light and matter become so inextricably linked so that the associated energy levels are altered. Although this phenomenon generally occurs between two separate objects or an object and its environment (such as an atom and a cavity), it can also occur between two different matter excitations inside the same object. Here, we observe self-strong coupling between localized surface plasmon resonances and the interband transition (IT) in aluminum nanorods. Aluminum nanorods are an ideal object for two main reasons. First, Al exhibits a spectrally localized IT in the visible [1]. Second, it can sustain surface plasmon resonances over a broad spectral range [2], whose spectral position can be easily tuned by changing the length of the nanorod [3] - akin to a classical optical cavity (Fig. 1).

Strong coupling is experimentally observed using optical spectroscopy and electron energy loss spectroscopy, and corroborated with numerical simulations. Interestingly, strong coupling is observed between the IT and multiple orders of the surface plasmon mode (dipole, quadrupole, hexapole). In each case the associated Rabi energy, which corresponds to the energy splitting between the two polaritonic branches, is retrieved. Finally, using a dedicated numerical model, we compute the generation rate of hot electrons in the nanoantenna. We show that hot electrons can be efficiently generated when the interband is strongly coupled with a plasmon resonance, offering potential applications for local photochemistry, and solar energy driven photocatalysis.



LSPR acting as the optical cavity  
Fig. 1: sketch of the IT-plasmon coupling

## References

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**Oraux**

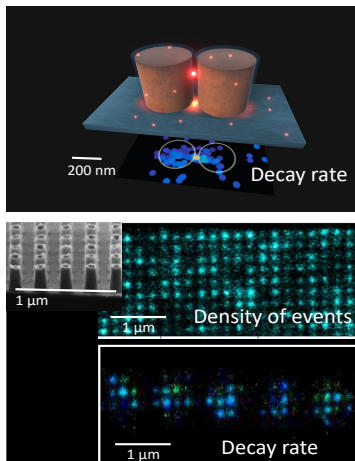
# Single-Molecule FLIM for light-matter interaction imaging at the nanometer scale

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Pushing light-matter interaction at the extreme with nanostructured materials and being able to measure such interaction is one of the major challenges of nanophotonics. To this aim, Single Molecule Localization Microscopy, which has been mainly applied to biological studies up to now, has become of great interest for the study of light-matter interaction in nanostructured materials, showing that the interaction between biophysics and nanophotonics can push forward the current technical limits and allow the study of new phenomena [1].



*Fig.1 Top: Super-resolved decay rate (inverse of the lifetime) map of single molecules labeling a GaP nanoantenna. Bottom: Super-resolved map in the near-field of an array of truncated gold nanocones (shown in the SEM image).*

We report on recent results obtained at Institut Langevin with smFLIM (single molecule Fluorescence Lifetime Imaging Microscopy), a novel technique that enables lifetime mapping of single molecules at the nanometer scale [2, 3]. smFLIM consists in multiplexed and super-resolved fluorescence lifetime imaging with single molecules with a field of view of  $\sim 10 \mu\text{m}^2$ , a localization precision of  $\sim 15 \text{ nm}$  [4, 5], and a temporal range spanning from ps to ms [2,3]. Since fluorescence lifetime is directly linked to the Local Density of Optical States (LDOS) of the nanostructured environment, we show that smFLIM can be used for LDOS imaging of disordered and deterministic nanostructures with extensions going from a few hundred nanometers to several microns, such as silver nanowires [4,5], dielectric nanoantennas (Fig.1 top) [2], and periodic arrays of hollow gold truncated nanocones (Fig. 1 bottom) [3].

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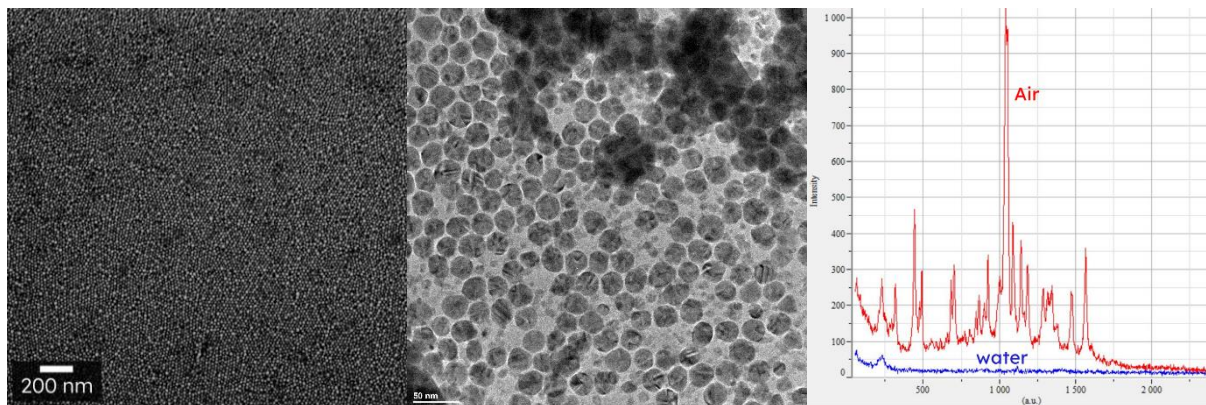
# High-Speed SERS: Unlocking Single-Molecule Reaction Insights

Samantha Roque and Jean-Christophe Valmalette

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The full spectral detection of single molecules presents numerous technical and scientific challenges due to their short-lived stochastic nature which begs for high-sensitivity, high-speed, and high-specificity acquisition. Single molecule detection was achieved by fluorescence 20 years ago and by Raman spectroscopy only 6 years later despite Raman's significantly smaller cross sections (9-14 orders of magnitude smaller compared to that of fluorescence). This advancement was made possible by using plasmonic nanostructures, primarily silver or gold, by the so-called single molecule surface-enhanced Raman spectroscopy (SMSERS). This extremely sensitive technique is highly sensitive to various factors such as molecular interaction, charge transfer, temperature, stress, orientation, etc. The ability to probe reactivity of molecules at the nanoscale is of great importance to investigate bacteria, viruses, biomolecules such as proteins, pollutants, materials, and more challenging systems such as the vibrational properties of water molecules at hydrophobic interfaces.



*Figure 1 Surfactant-free film consisting of ~15 nm AgNP monolayers (left), TEM of film showing very small AgNPs (~2.5 nm) scattered between bigger AgNPs (center), and real-time stochastic SERS in air and water (10 $\mu$ W, 250 ms acquisition time) (right)*

The strong enhancement involved in SMSERS results from the combination of electromagnetic and chemical effects. In the former, the nanostructure behaves as an optical nano-antenna in the visible range, while the latter, although less understood, is believed to be involved on surface electronic states resulting from the interaction of the molecule with surface defects, such as clusters or adatoms. Our group developed a new strategy to stabilize surface defects on silver nanoparticles and to investigate the mechanism of chemical enhancement to get high-speed SERS detection.



# Control of heat anisotropy and Chemical degradation at the nanoscale.

Marlo Vega<sup>1,2,3</sup>, Paul-Ludovic Karsenti<sup>1,3</sup>, Julien Moreau<sup>2</sup>,  
Michael Canva<sup>1,3</sup>, Paul Charette<sup>1,3</sup>, Jean-François Bryche<sup>1,3</sup>

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By absorbing and converting light into heat, metal nanoparticles behave as heat sources that could be used in many fields like biosensors or photocatalysts.

In this work, we first investigate the photothermal heating of asymmetric nano-crosses by ultrashort light pulses. We focus on gold crosses on gold film atop a glass substrate. Samples are fabricated by e-beam lithography [1,2]. The crosses are 300/410 nm lengths, 60 nm height, 60 nm width with periods 530-640 nm. We show experimentally and numerically that non-thermal energy density and temperature inside the two arms of the crosses can be controlled with the polarization of the pump pulse, letting us to adjust optical delay. We also demonstrate the importance of considering non-thermal electron ballistic displacement to reproduce the measured experimental data in pump-probe spectroscopy [2].

Secondly, we investigated photodegradation phenomena. We report a new method for patterning and imaging surface chemistry with nanoscale resolution. It relies on precisely controlling the electronic temperature distribution on and around gold nanostructures on a gold film generated under pulsed illumination (Fig1). This localized photothermal degradation can be used for sensing applications where molecules need to be localized only in areas of high electric field [3].

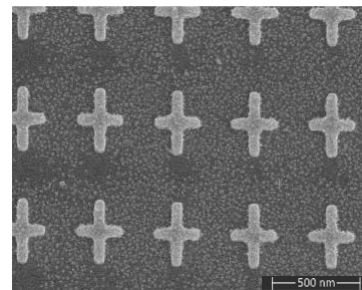


Figure 1. SEM pictures of local degradation induced by pulse light between gold nanocrosses.

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# Plasmonic Au-nanocatalysts for the n-dealkylation of amines

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Plasmonic material such as plasmonic nanoparticles (NPs) are highly relevant materials for catalysis. The localized surface plasmon (LSP) is a collective oscillation of the free electrons confined inside metallic NPs induced by the interaction with light which generates highly excited electrons. It can have several effects on the local environment such as inducing a local increase of the electromagnetic field (enhanced field) and the temperature (thermoplasmonic effect) or generating hot electrons. As catalytic reactions need a high temperature or an electron transfer to be initiated, both effects can be exploited to induce a LSP mediated catalytic reaction[1]. Among the numerous catalytic reactions existing, the N-dealkylation of amines is an interesting process and can involve a coordinated porphyrin as a catalyst[2],[3]. The main issue for this reaction is the heat required to cross the energetic gap.

The aim of this work is to prepare a metal porphyrin catalyst bearing a thiolated or pyridine anchoring group to be grafted onto plasmonic gold nanoparticles. The idea is to combine a traditional catalyst with plasmonic nanomaterial to enhance the rate of the reaction without any heat and provide the a plasmon mediated molecular catalyst for the N-dealkylation of amines. Such a method could be a solution to the problem of water contamination by opioids (figure 1, right).

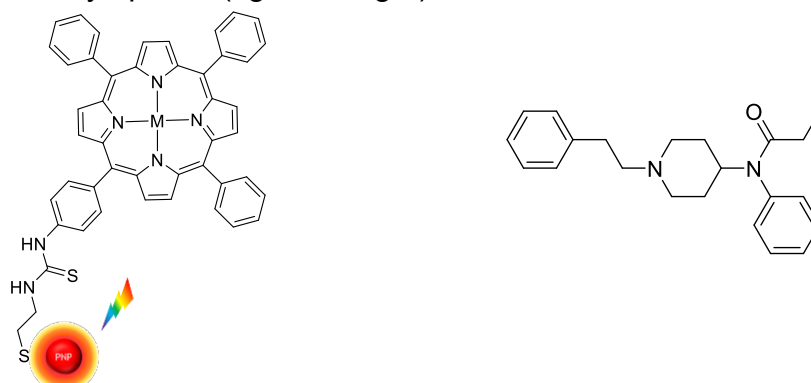


Figure 1. Structure of the nanocatalyst synthesized in this work for plasmon mediated molecular catalysis (left) and the fentanyl molecule, a powerful synthetic opioid analgesic (right)

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# Plasmonic Dark-field Microscopy for Real-time Tracking of Protein Corona Formation on Single Nanoparticles

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For many applications in nanomedicine, nanomaterial injection directly into biological fluids is requested. The spontaneous interaction between these nanomaterials and the proteins present in such fluids leads to the formation of a shell known as “Protein Corona” (PC).<sup>1</sup> The formation of PCs undeniably results in changes of the physico-chemical properties of nanoparticles, and thus reduces their targeting efficiency. It is therefore essential to fully understand the mechanisms of PC formation in order to predict their future behavior and hence optimize their design.<sup>2</sup>

Here we introduce a method which combines dark-field microscopy with a microfluidic system to track the formation of PC in-situ, at the single particle level.<sup>3</sup> The use of a total internal reflection configuration enables the monitoring of protein adsorption on the surface of nanoparticles directly in undiluted blood serum without being affected by background signal. The method, which relies on changes in scattering, provides a way to investigate plasmonic particles with millisecond temporal resolution without the need for a spectrometer. Timetraces, giving access to adsorption kinetics and final spectral shifts, combined with electromagnetic simulations were used to quantify the adsorption kinetics. The versatility of the method opens up the possibility of extending the scope of the study to other types of materials, structures or functionalities to relate the formation of PC's to the performance of particles in biosensing applications.

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# Plasmonic and Photonic Refractive Index Biosensor Based On Bound States In The Continuum

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Bound states in the continuum (BICs) were first demonstrated theoretically in 1929 by von Neumann and Wigner [1]. BICs can be assigned to three categories [2]: (i) symmetry-protected BICs (SP-BICs), (ii) accidental BICs, and (iii) Friedrich-Wintgen BICs (FW-BICs). In 2008, the concept of BICs was realized for the first time in photonic systems, and since then it has been growing interest in various applications [3]. The unique properties of BICs have led to a wide range of applications in acoustics, photonics, and then were developed in plasmonics [4]. In this work, we propose a novel structure for biosensors based on a diffraction grating to diagnose four types of cancers cells. This biosensor is used to detect Hela, Jurkat, PC12, MDA-MB-231 and MCF-7 cancerous cells, based on their refractive indices. The present configuration consists of a glass layer covered by a gold layer, a grating coated by a silicon nitride layer separating the sensor from sensing medium. Here, numerical analysis based on the Rigorous coupled-wave analysis method (RCWA) [5] is performed to optimize the biosensor sensitivity (S), by also considering the full width at half maximum (FWHM), detection accuracy (DA), and figure of merit (FoM).

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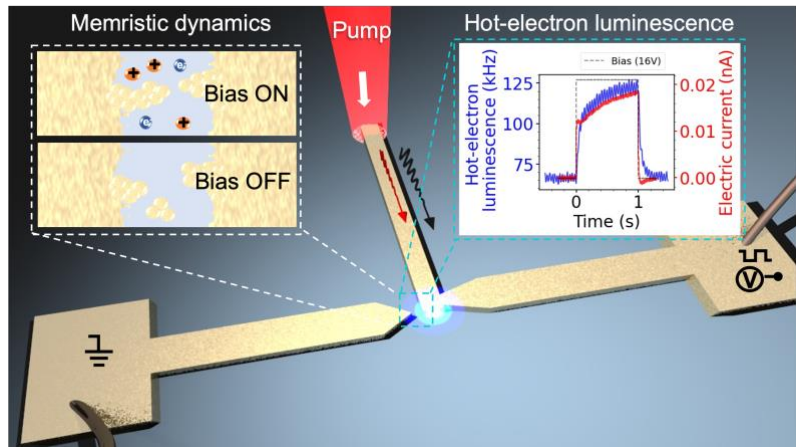
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# Memristive Control of Plasmon-Mediated Nonlinear Photoluminescence

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Nonlinear photoluminescence (N-PL) is a broadband photon emission arising from a nonequilibrium heated electron distribution generated at the surface of metallic nanostructures by ultrafast pulsed laser illumination [1]. N-PL is sensitive to surface morphology, local electromagnetic field strength, and electronic band structure, making it relevant to probe optically excited nanoscale plasmonic systems. It also has been key to accessing the complex multiscale time dynamics ruling electron thermalization [2]. Here, we show that plasmon-mediated N-PL emitted by a gold nanowire can be modified by an electrical architecture featuring a nanogap [3]. Upon voltage activation, we observe that N-PL becomes dependent on the electrical transport dynamics and can thus be locally modulated. This finding brings an electrical leverage to externally control the photoluminescence generated from metal nanostructures and constitutes an asset for the development of emerging nanoscale interface devices managing photons and electrons.



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# Femtosecond drift photocurrents generated by an inversely designed plasmonic antenna

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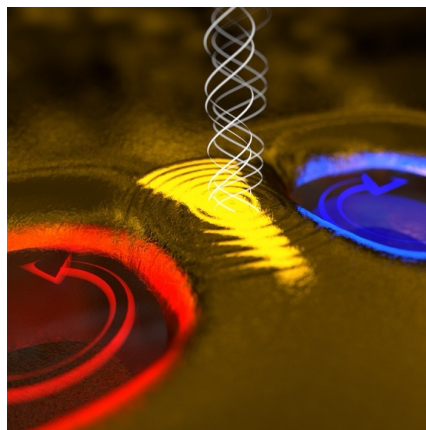
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Photocurrents play a crucial role in various applications, including light detection, photovoltaics, and THz radiation generation. Despite the abundance of methods and materials for converting light into electrical signals, the use of metals in this context has been relatively limited. Nanostructures supporting surface plasmons in metals offer precise light manipulation and induce light-driven electron motion. Through inverse design optimization of a gold nanostructure, we demonstrate enhanced volumetric, unidirectional, intense, and ultrafast photocurrents via a magneto-optical process derived from the inverse Faraday effect [1]. This is achieved through fine-tuning the amplitude, polarization, and their gradients in the local light field. The virtually instantaneous process allows dynamic photocurrent modulation by varying optical pulse duration, potentially yielding nanosources of intense, ultrafast, planar magnetic fields, and frequency-tunable THz emission. These findings open avenues for ultrafast magnetic material manipulation and hold promise for nanoscale THz spectroscopy.



**Figure 1.** Illustration of a plasmonic nanostructure designed by an inverse optimization to manipulate the light field and polarization at the nanoscale in such a way that a volumetric, unidirectional, intense, and ultra-short photocurrent emerges.

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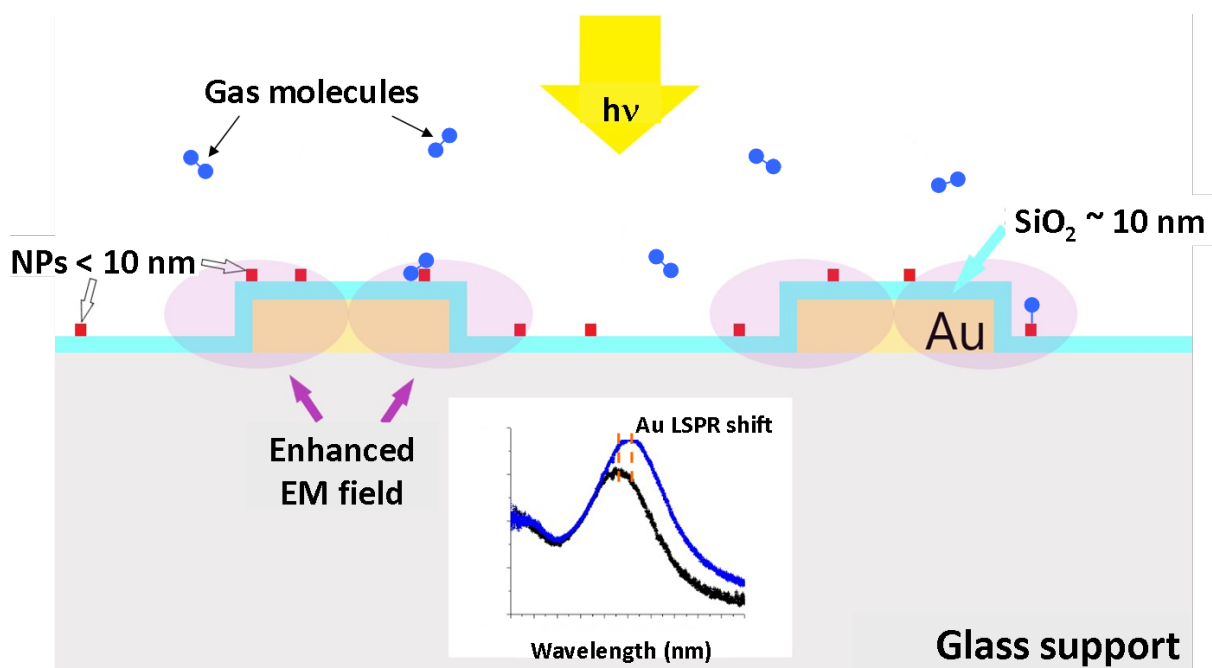
# Nanoplasmonic sensing

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Gold nanodisks are very effective plasmonic sensors. This is especially true when gas molecules adsorb onto or interact with them. This interaction alters the local dielectric properties and induces a wavelength shift in the gold localized surface plasmon resonance (LSPR) (see figure).



We used nanoplasmonic sensing (NPS) to investigate the interactions of various gas molecules with both bare and coated gold disks, as well as with nanoparticles or small atomic clusters supported on them. NPS is highly sensitive, quantitative, and non-destructive, which makes it well-suited for studying a wide range of gas pressures and temperatures.

# Enhancing Surface Plasmon Resonance Imaging Sensitivity to micro-RNAs

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In modern medicine, the need for rapid, reliable, and personalized point-of-care diagnostics for patients continues to grow. In the case of organ donation, a brain-deceased organ donor requires in-depth monitoring of his physiological conditions and adequate treatment to prevent the degradation of the tissues<sup>[1,2]</sup>. One way of tracking this degradation is to follow the evolution of the inflammatory response (i.e. cytokine storm) occurring throughout the patient's body thanks to specific biomarkers, particularly miRNAs<sup>[3]</sup>. Here, we propose using a Surface Plasmon Resonance Imaging (SPRI) biochip system to quantitatively detect those miRNAs and follow the course of the cytokine storm. Classical methods for detecting miRNAs like PCR protocols or northern blotting are time consuming. SPRI offers several advantages: multiplexing of targets, rapid measurements in complex media, and quantitative measurement of biomarkers. The limit of detection (LOD) for SPRI biosensors is typically in the nanomolar range for a 20-bases single-stranded DNA after a few minutes detection step<sup>[4]</sup>. However, the miRNAs targeted for detection in this study are only present in the high femtomolar range, necessitating a reduction in the LOD by at least four orders of magnitude.

To achieve this objective, we employed various strategies. We focused our work on optimizing the surface chemistry to maximize the affinity between our targets and the bioreceptors. We have shown that the thiol composition of the self-assembled monolayer and the nature of the capture probe on the biochip gold surface can be tuned to maximize the capture of miRNAs at low concentrations. Subsequently, we worked on increasing the shift in the refractive index following the hybridization step with a sandwich like assay using gold nanoparticles (AuNPs). These AuNPs were synthesized at ambient temperature using a one-step process. In parallel, we are exploring nanostructuring the biochip itself to enhance the plasmonic signal by combining localized surface plasmons with propagative ones<sup>[5]</sup>. The femtomolar range objective of detecting those miRNAs was achieved with these combined improvements.

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# Can the plasmon resonance of a nanoparticle be measured using a scanning probe microscope?

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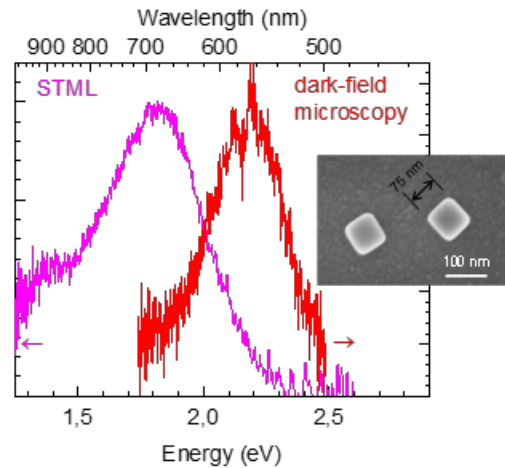
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Probing the optical properties of plasmonic nanoparticles (NPs) on the nanometer scale has become crucial in nanophotonics, e.g., to engineer their near-field coupling to other plasmonic NPs or to quantum emitters. Various techniques have been developed to carry out such investigations, either using photons or electrons to excite the plasmon modes. However, near-field techniques based on scanning probe microscopy have been reported to affect the plasmon resonances of the NPs, which can lead to incorrect assignment to plasmon modes known from other techniques [1,2]. In this talk, we report on the scanning tunneling microscopy-induced luminescence spectra (STML) of individual plasmonic NPs measured in air. When compared to the results of far-field light scattering measured under the same ambient conditions, the STML measurements show spectral shifts and peak broadening of hundreds of meV. We simulate the near-field excitation and the effect of the tip using the finite-element method and show that these effects alone cannot explain the spectral shifts and peak broadening observed for STML experiments in air [3]. Our results may help in understanding the spectral shifts and peak broadening observed in virtually any optical measurement using a scanning probe microscope operated in air, where an emitter is located in the tip-sample gap or the tip-sample nanocavity emits light to the far field.



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# Probing thermophoretic forces near plasmonic structures using optical tweezers

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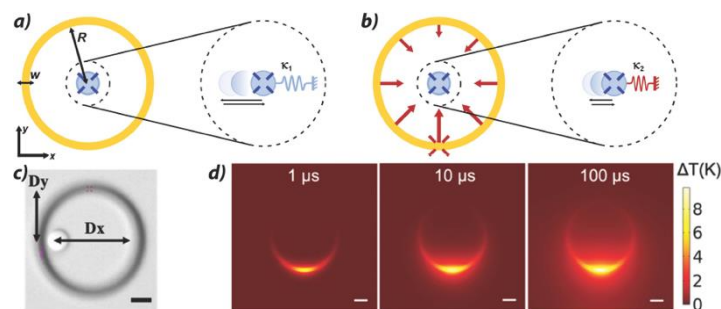
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Despite optical tweezers are systems of great interest for manipulation of single particles, they are not efficient for trapping particles at the nanoscale. By combining optical tweezers with plasmonic structures, a more localized and stronger trap becomes possible, namely plasmonic nano-tweezers. [1-2] However, being able to strongly enhance local electrical fields, the plasmonic heating is often generated near the nanostructures, leading to various unwanted thermal effects, including thermophoretic force. Understanding the thermophoretic force acting on individual structures is essential for various applications in nanotechnology and biophysics, and is still a challenge to this day. [3-5]

We propose a new approach using dual-beam optical tweezers to probe these forces locally, combining direct force measurements, an analytical harmonic model and numerical simulations. By conducting thorough experimentation and simulation, we investigate how the thermophoretic force, acting on polystyrene beads trapped in gold nanostructures such as nanorings in the Figure, varies with factors such as temperature gradients, with a significant emphasis on its correlation with the distance from the gold structure.



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# Surfactant-Free Plasmonic SERS Ag Nanostructures

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In this research, we create surfactant-free silver nanostructures that are suspended at the water/hydrophobic boundary. Removing surfactants is crucial for unobstructed observation of the plasmonic properties of AgNPs, especially when aiming for highly sensitive surface-enhanced Raman spectroscopy (SERS) measurements.

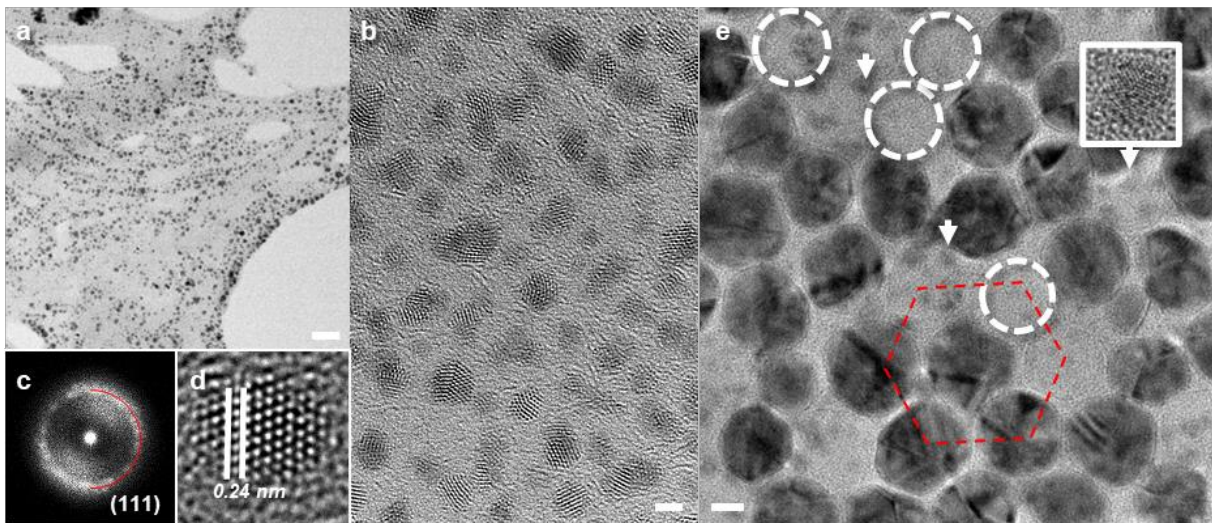


Figure 1 (a) TEM image of self-suspended silver film (scale bar 50 nm), (b) HRTEM details of this film showing AgNPs embedded in amorphous layer (scale bar 2 nm), (c) fast Fourier transform (FFT) of the full image (b) showing a ring at  $4.2 \text{ nm}^{-1}$  corresponding to (111) interplanar distance, (d) HRTEM image of a single AgNP, (e) AgNPs in hexagonal close packing and highlighted circles in amorphous interparticle areas (scale bar 10 nm).

To achieve the required high purity, we developed a novel synthesis method that produces freestanding, surfactant-free silver nanostructures. Monodispersed AgNPs ( $d=15 \text{ nm}$ ) organized into domains were observed through scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) confirmed the films are composed of pure silver. Transmission electron microscopy (TEM) showed even smaller AgNPs ( $d \approx 2.5 \text{ nm}$ ) that did not coalesce under the beam embedded in an fluid-like amorphous layer. These silver nanostructured films with small AgNPs and close interparticle distances enhances the plasmonic properties important for SERS measurements. Using these films, we observed stochastic SERS spectra with well-defined peaks that could suggest single-molecule detection.

# Self-assembly of metal nanoparticles: assessing the role of plasmonic coupling

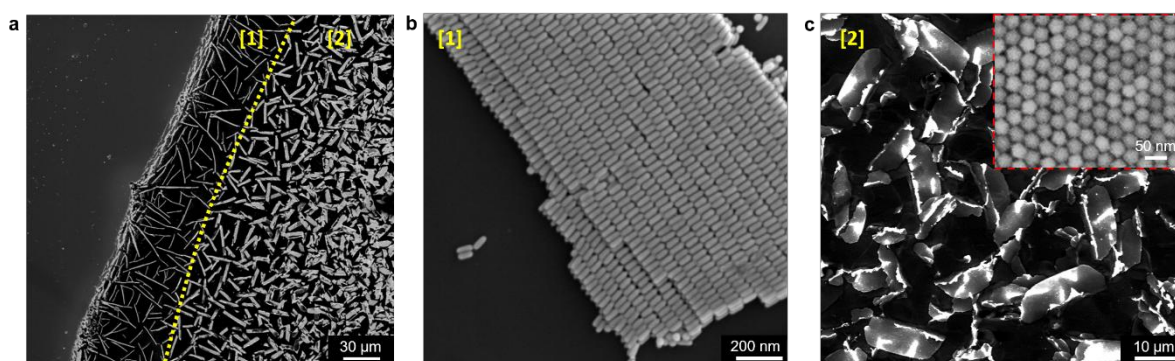
**C. Brissaud<sup>1\*</sup>, L. V. Besteiro<sup>2</sup>, M. Comesaña-Hermo<sup>1</sup>, and J.-Y. Piquemal<sup>1</sup>**

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In this work we explore the self-assembly of anisotropic metal nanoparticles (NPs) into plasmonic supercrystals (SCs) and their application as heterogeneous photocatalysts.<sup>1</sup> These assemblies are of growing interest due to their unique collective optical properties, particularly their ability to concentrate electromagnetic fields in the nanogaps between particles.<sup>2</sup> This enhancement is expected to confer novel photocatalytic properties distinct from those of individual NPs, potentially improving catalytic efficiency. We investigate SCs made from Au and core-shell Au@Pd nanorods (NRs), examining their photocatalytic activities across various organic transformations. Notably, the assemblies of Au NRs are implemented as photocatalysts for the dimerization of aniline which unexpectedly resulted in a polymerization reaction, while the Au@Pd structures prove effective in cross-coupling reactions, achieving good photocatalytic efficiencies. In addition, the use of Raman spectroscopy allows us to follow the reactivity of these materials at the micrometric scale and in *operando* conditions. Our findings underscore the versatility of plasmonic SCs as recyclable photocatalysts, with properties that can be tailored by adjusting the composition of the building blocks.



**Figure 1.** a) Low-magnification SEM image of the edge of a deposit. b, c) Enlarged SEM images of region [1] and [2] showing horizontally and vertically standing assemblies of NRs, respectively.

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# Lattice modes engineering based on bi-material arrays of metallic nanoparticles

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When the metallic nanoparticles are organized as arrays, one can observe a diffraction phenomenon which makes it possible to couple all the nanoparticles together and to reduce the damping of their LSPR. This collective resonance, called Surface Lattice Resonance (SLR), takes place when the LSPR is coupled to an in-plane (grazing) diffraction order<sup>1</sup>. This sharp resonance is very interesting for many applications like emission enhancement in LEDs or in biomedical imaging. However, if the metasurface is based on one metallic material, the spectral range of its optical response is limited. By means of numerical simulations and extinction measurements, we studied the spectral response and more precisely the lattice modes supported by gold (Au), aluminum (Al) and quincunx gold-aluminum (Au-Al) gratings in the visible range (Fig. 1). The goal is to understand the role played by gold and aluminum nanoparticles (NPs) in bi-material arrays, how they contribute to the coupling between Localized Surface Plasmon Resonances and Rayleigh Anomalies to form Surface Lattice Resonances. Finally, the work delves into fundamental mechanisms governing the optical behavior of plasmonic bi-material NPs arrays, with a specific emphasis on their application to fluorescence enhancement applications. By understanding these interactions, we aim to optimize the design of bi-material NP arrays to enhance the performance of fluorescence quantum dots.

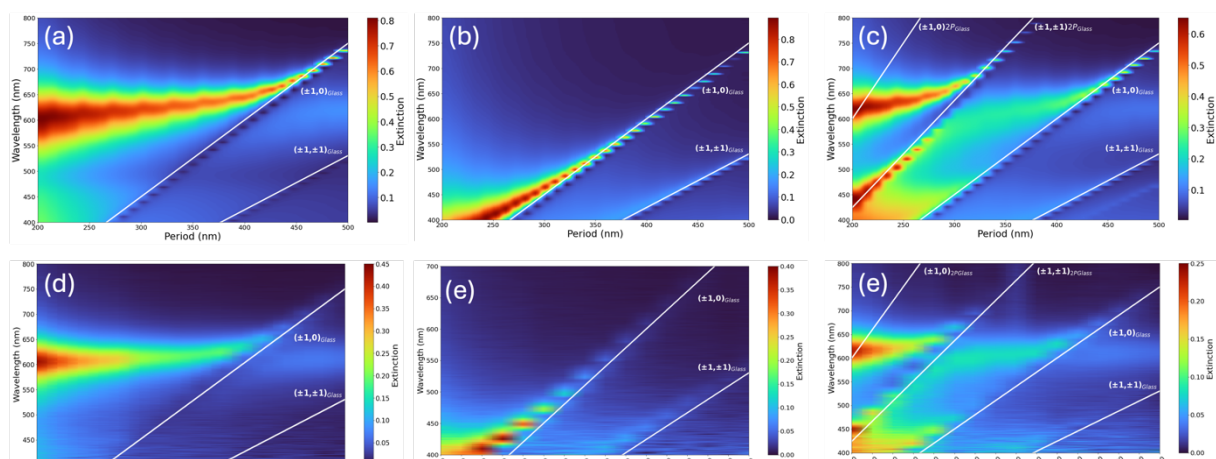


Figure 1: Dispersion maps built from simulated (a, b, c) and experimental (d,e,f) extinction spectra recorded as a function of the period of a gold (a and d), an aluminum (b and e) and a gold-aluminum square array. The particle diameters are set to 80 nm.

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# Plasmonic properties of asymmetric gold nanocylinder grating

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In this study, we investigate the influence of symmetry breaking in nanocylinder gratings on plasmonic properties and its impact on surface-enhanced Raman scattering (SERS) performance. We alter the symmetry by adjusting the grating period in one direction, transitioning from a square grating to a rectangular one, which changes the symmetry group from  $C_{4v}$  to  $C_{2v}$ . This symmetry reduction leads to a redshift and narrowing of the plasmon resonance due to the coupling between the plasmon and a diffraction order of the grating. Remarkably, we demonstrate that this coupling occurs regardless of the polarization direction. Additionally, we show that the SERS efficiency of these plasmonic substrates is higher for gratings with reduced symmetry, attributed to the narrower full width at half maximum (FWHM) and the higher quality factor of the surface plasmon resonance.

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# Posters

# Radiolytic synthesis of gold nanoparticles stabilized by NIPAM monomers or polymers and applications in photo-catalysis

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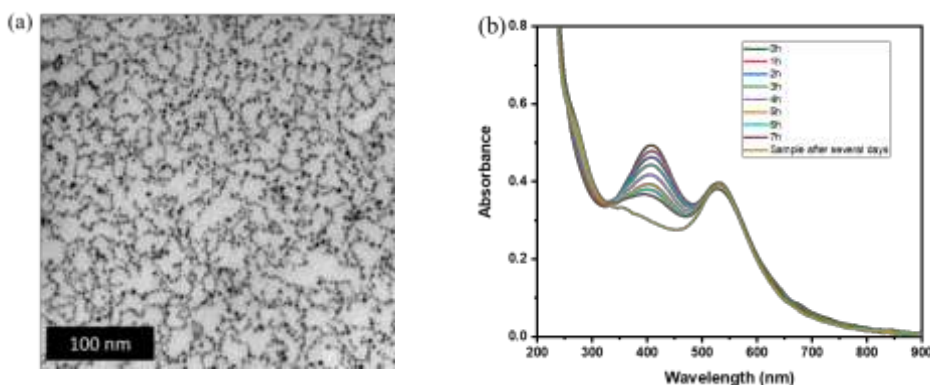
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Metallic nanoparticles (MNPs) arouse a growing interest due to their versatility, which is attributed to their unique properties (such as optical properties) influenced by their size, shape, and composition. These unique optical properties stem from localized surface plasmon resonance.

Environmentally friendly synthesis methods and effective stabilization agents are essential for fabricating MNPs with controlled sizes and shapes. Among the available methods, radiolytic synthesis based on irradiation by ionizing radiations is powerful; no chemical reactants are needed as the reducing species (solvated electron, radicals) are generated from the solvent [1]. This study explores the radiolytic synthesis method, along with the use of a thermosensitive polymer, Poly(N-isopropylacrylamide) (PNIPAM), and its monomer, N-isopropylacrylamide (NIPAM), for the stabilization of gold nanoparticles (AuNPs) in aqueous solutions.

The radiolytic reduction of gold metallic salts in the presence of PNIPAM or NIPAM in aqueous solutions leads to the formation of small spherical AuNPs with high stability at room temperature (Figure 1a). The synthesized PNIPAM-AuNPs and NIPAM-AuNPs demonstrated efficient photocatalytic activity under plasmon excitation for the degradation of 4-nitrothiophenol (4-NTP), a model pollutant (Figure 1b).



**Figure 1.** (a) TEM micrograph of NIPAM-AuNPs synthesized by radiolysis (b) absorption spectra monitoring the photocatalytic degradation of 4-NTP by plasmon excitation of NIPAM-AuNPs

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# Engineering aluminium metasurfaces for high quality factor devices within a large spectral range

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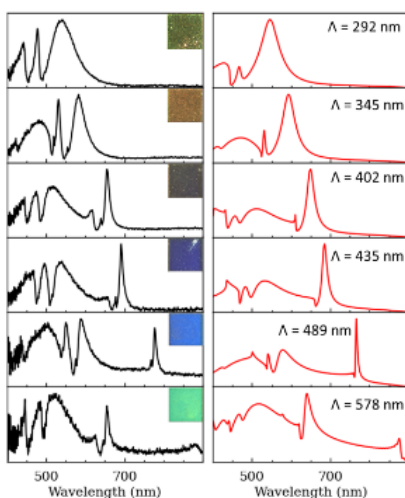
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Aluminum, although less explored than the commonly used gold or silver nanoparticles (NPs) in plasmonics, presents several advantages. This metal is not only cost-effective but also exhibits an optical response driven by the excitation of localized surface plasmon, enabling it to cover a broad spectral range from the ultraviolet (UV) to the near-infrared (NIR). However, aluminum NPs are hindered by low quality factors, particularly in the visible range ( $Q \sim 2$ ), due to significant electron damping. This intrinsic loss broadens the resonance, limiting their effectiveness in applications such as detection and color filtering. For example, detecting small changes in the surrounding medium, like the presence of an analyte, becomes difficult with a broad resonance. Similarly, effective color filtering requires a narrow resonance to isolate specific wavelengths, which is not feasible with the typically broad resonance of aluminum NPs.

The primary goal of this work is to enhance the quality factor of aluminum structures. We propose arranging the NPs in a regular, periodic pattern as shown in figure 1, which leverages strong long-range interactions to generate a narrow resonance known as surface lattice resonance [1]. Using this approach, we achieved unprecedented quality factor values ( $Q \sim 110$ ) in air, highlighting the crucial role of long-range interactions between NPs (fig. 1).



Moreover, aluminum NP arrays exhibits higher-order diffracted modes that are significantly more pronounced than those observed in gold and silver NPs [2], a result of aluminum's lower absorption capacity. This allows for the generation of a broader range of wavelengths in the visible spectrum compared to gold or silver, opening up new possibilities for various plasmonic applications in nano optics.

Fig 1 : On the left experimental extinction spectra of aluminium arrays with different grafting constant. On the right, the corresponding FDTD calculations.

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# Tuning of Plasmonic Surface Lattice Resonances: On the Crucial Impact of the Excitation Efficiency of Grazing Diffraction Orders

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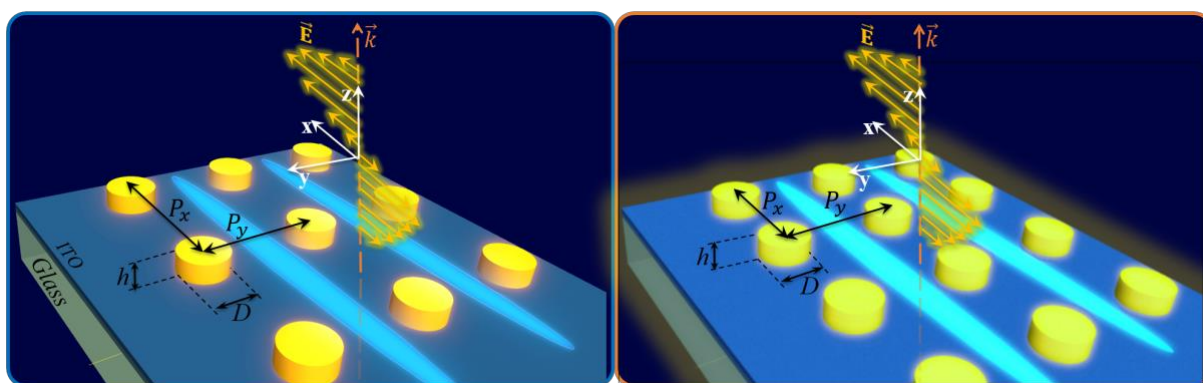
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Metallic nanoparticles exhibit remarkable optical properties through localized surface plasmon (LSP) resonances. When arranged in arrays, nanoparticles form surface lattice resonances (SLRs) affected by inter-particle distance. SLRs can offer narrower bandwidths and stronger electric field enhancements than LSP modes, crucial for efficient optical device development. Among important aspects, grazing diffracted orders crucially impact SLR properties, facilitating long-range nanoparticle interactions. This study explores how these photonic modes propagating at the substrate surface influence SLRs, using experimental and theoretical approaches, including Finite Difference Time Domain simulations on gold disk arrays. Results show SLR properties strongly rely on diffracted mode efficiency controlled by the grating constant along the incident polarization. Notably, large inter-particle spacing along the incident polarization can strongly reduce the SLR red-shift. Understanding and managing long-range interactions in engineered plasmonic structures are highlighted, providing insights for enhanced performance in advanced photonic and optoelectronic devices.<sup>1-3</sup>



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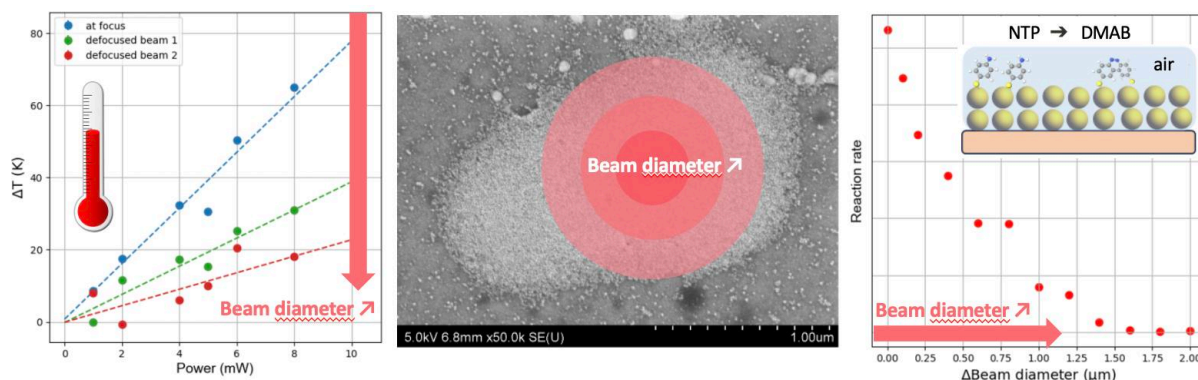
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# 4-Nitrothiophenol to DMAB reaction: Photothermal vs photochemical mechanisms

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Plasmon-enhanced photocatalysis has garnered significant attention for its potential to increase chemical reaction selectivity and efficiency [1]. Recent efforts have focused on identifying procedures for distinguishing photochemical from photothermal contributions in various reactions [2]. Here, we report a survey of a widely used hot electron model reaction —the transformation of nitrothiophenol (NTP) to p,p'-dimercaptoazobenzene (DMAB) [3] — on self-assembled colloidal Au nanoparticles (NPs) in both air and aqueous media. We investigated the plasmon resonance of the clusters, the local temperature under resonant 638 nm laser irradiation using A-Stokes thermometry, and evaluated the reactivity using Surface Enhanced Raman Scattering (SERS). Our analysis focused on their dependence on the illumination area, as behaviors are expected to differ for photothermal and photochemical mechanisms. We discuss the trends observed for the local temperature and the reaction rate on the laser beam diameter, which indicate a primarily photothermal effect for the reaction in air (Figure 1). Experiments in aqueous media proved more challenging to interpret due to lower reproducibility of the SERS signal. We discuss the reaction mechanisms in both environments, and where optical probe can be useful for discriminating the underlying mechanisms of plasmonic photocatalysis.



*Figure 1: Evolution with laser beam diameter of local temperature increase upon irradiation from A-Stokes thermometry as a function of optical power (left) and reactivity at constant optical power from SERS (right) for the NTP to DMAB reaction on Au NPs clusters (center) .*

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# Optical and structural characterization of core-shell nanomaterials( $\text{SiO}_2@\text{TiO}_2@\text{AuNPs}$ and $\text{SiO}_2@\text{AuNPs}@\text{TiO}_2$ ) for $\text{H}_2$ production

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Hydrogen is one of the potential clean energy sources that could address two major worldwide concerns: energy crises and environmental difficulties. Hydrogen production often involves the use of fossil-based technologies, which emit a significant amount of greenhouse gases in the process. As a result, one of the primary objectives of the last several decades has been to decarbonize the industry. Finding affordable, environmentally friendly, and dependable hydrogen generation systems with minimal emissions is essential for achieving this goal [1]. At the Institut de Chimie Physique d'Orsay (ICP), we found a promising way to increase the yield of  $\text{H}_2$  production taking profit of a core-shell structure with two different configurations ( $\text{SiO}_2@\text{TiO}_2@\text{AuNPs}$  and  $\text{SiO}_2@\text{AuNPs}@\text{TiO}_2$ ) [2]. However, the difference in  $\text{H}_2$  yield between these two structures remains unknown and requires in-depth investigation. Using optical techniques such as surface sensitivity SFG spectroscopy can help track and monitor the steps involved in  $\text{H}_2$  production at the surfaces of these structures. SFG spectroscopy is an *in-situ* optical probe that has succeeded in monitoring *in-situ* interfaces [3]. Therefore, we use the same approach on these core-shell nanomaterials to provide an exact pathway to the chemical reactions that occur during  $\text{H}_2$  production. The core-shell nanomaterials have been synthesized and studied, and the coating optimized for SFG spectroscopy. We have used different deposition techniques (USP coating and spin coating) and substrates. Additionally, we have characterized the samples using spectroscopy techniques and SEM imaging to better understand the chemical and structural properties of these materials. At the end, our findings could potentially pave the way to have a coupled fundamental view of *in-situ* surface chemistry and could impact the field of green energy production.

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# Measurement and control of the spectral shift of dimers and small aggregates of plasmonic gold nanoparticles

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Plasmonic gold nanoparticles have been extensively studied for their optical properties used in different applications such as nanophotonics, photocatalysis or advanced cancer therapies. These nanostructures are characterized by the local surface plasmon resonance, that gives rise to their ruby red signature. The growing interest for gold nanoparticles has been motivated by the development of synthesis as well as instrumentation for the study of their optical properties. In this direction, hyperspectral dark-field microscopy is able to spatially localize single nanoparticles directly on a substrate while simultaneously measuring their spectrum, providing a useful tool for the detection of local interactions between particles [1]. These interactions can vary quite significantly depending on the distance between nanoparticles in a film made of gold nanoparticles on a substrate, considerably affecting the colors of the nanoparticles. In this poster, we present a study by hyperspectral dark-field microscopy of films made of 50 nm diameter sized spherical gold nanoparticles [2] dropcasted on glass. In order to reduce the interactions at the nanoscale, silica shells of different thickness (from 15 to 50 nm) have been grown [3]. Correlations between hyperspectral microscopy and AFM are made to highlight how the presence of the shell affects the spectra of single particles, dimers or aggregates.

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# Characterization of quantum emitters

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The single-photon emitters play a crucial role in applications of quantum technology, such as quantum metrology, quantum communication and in the field of biology<sup>[1, 2]</sup>. In this study, we focus on the characterization of quantum emitters in diamond, specifically the germanium-vacancy (GeV), Silicon-vacancy (SiV) and nitrogen-vacancy (NV) centers, which are interesting candidates for single-photon sources<sup>[3, 4]</sup>. Our home-built microscopy setup includes an inspection camera and a spectrometer for photoluminescence studies. The setup allows for detailed characterization of the optical properties of the GeV, SiV, NV centers and quantum dots, highlighting their distinct emission characteristics, as shown in the figure below.

Additionally, we present data from optically detected magnetic resonance (ODMR) to probe the magnetic properties of the NV centers. The ODMR results offer detailed insights into the zero-field splitting and Zeeman splitting, advancing our understanding of the spin dynamics in NV centers and their application in magnetic field sensing<sup>[5]</sup>.

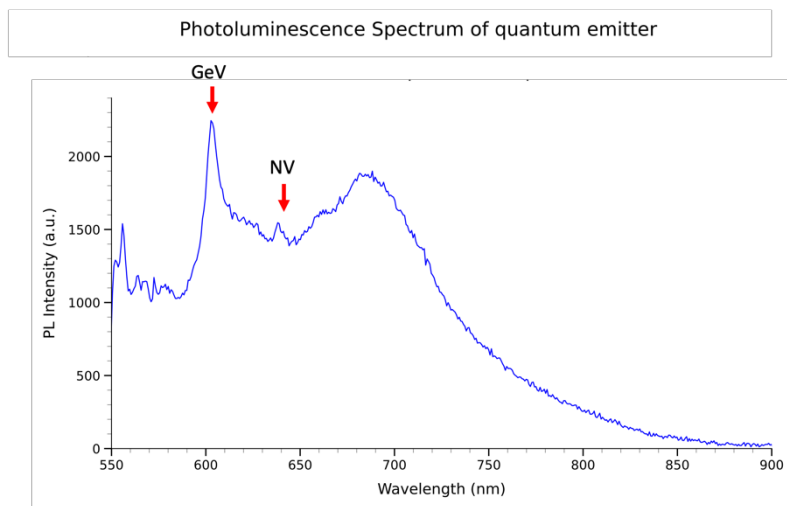


Figure Photoluminescence spectrum from nanodiamond emitters

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# Plasmonic nanostructures and films for biosensing, light nanosources and ultrafast thermal applications

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Plasmonics has a wide range of applications, from biomedical and environmental sensors to light emission control.

Through several projects, we have studied plasmonic couplings, especially those between propagative plasmons in metal films and localized plasmons in nanostructures. The resulting hybrid mode [1,2] has demonstrated its interest in biosensing applications, notably in SPR and SERS (Raman spectroscopy) [3,4]. The presence of nanostructures on a gold film also allows better control of plasmon propagation distances at interfaces, by increasing their confinement. This is particularly useful for improving imaging resolution (10um to 500nm) for the study of cells [5], for example. In the field of light sources, the issue of emission and direction control can be addressed through the addition of plasmonic nanostructures. Fabrication is also a key point, since it strongly modifies plasmonic properties (roughness, porosity, shape and size particles). Thus, we have studied UV-Nanoimprint [2] and also developed an abrasive-free chemical-mechanical planarization (CMP) process [6] that produces structures as good as or even better than lift-off and which is industry-compatible.

Finally, in terms of thermal properties, we have demonstrated with pump-probe spectroscopy measurements and numerical modeling, how temperature can be controlled with nanometric resolution and over sub-picosecond time windows [7,8].

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# Plasmonic two-photon photopolymerization for strongly-coupled nanosources of light

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Nowadays rapidly increasing data traffic requires more efficient energy and information exchange methods. Integrated optics and nano-optics with advanced optical nano-source is the most prominent solution. In this context, we aim to develop a hybrid nano-emitter sensitive to an external polarization and based on the strong coupling between metal nanoparticles and semiconducting nanoplatelets (NPLs) of which the spatial distribution overlaps well with the involved plasmonic modes.

To control the nanoscale anisotropic spatial distribution of NPL(s) relative to the metal nanoparticles, polymer made by plasmon-induced 2-photon photopolymerization is employed [1]. Through applying different energies and wavelengths of the incident laser, the size of printed polymer around gold nanotriangles (AuNTs) can be manipulated. This allows us to control the distance between NPLs and AuNTs as NPLs are embedded in the polymer or attached on polymer surface. Furthermore, AuNTs geometry parameters (height, edge length and corner rounding radius) were investigated to realize the spectral overlap between NPLs PL and AuNTs LSPR.

Besides, the alignment of the NPL dipole moment with a strong electric field in a plasmonic cavity is possible to be done by pre-applying a light or a DC field [2]. These first studies pave the way to achieve strong coupling with Rabi-energy  $> 500$  meV as well as reliable on-demand single-photon sources.

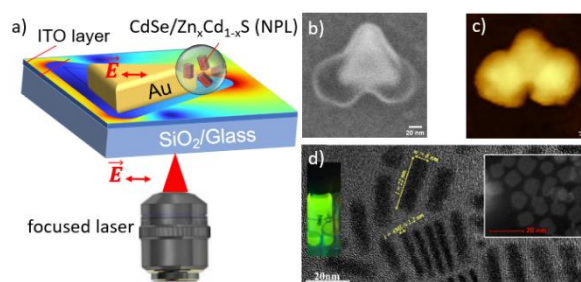


Figure 1: a) Near-field two-photon photopolymerization illustration; b) SEM picture and c) AFM image of a nanotriangle after photopolymerization; d) Excited NPLs solution and TEM images of NPLs

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