

GDR Groupement
De recherche

Plasmonique Active et Photo-Electro-Stimulation

JOURNEES PLENIERES 2022

Le Mans Université

ABSTRACT BOOK

01 & 02 Juin 2022



Contact :

<https://gdr-pse-pa-2022.sciencesconf.org/>



GDR

Groupement
de recherche

Plasmonique Active

OXFORD
INSTRUMENTS

WITec
focus innovations



Le Mans
Université



IMMM
Institut des Molécules
et Matériaux du Mans
Le Mans Université
UMR CNRS 6283

Mot d'introduction

Chères et chers collègues,

Nous sommes ravis de vous accueillir aux journées plénières communes aux GDR *Plasmonique Active* et *Photo-Electro-Stimulation*. Ces journées se tiendront à l'Université du Mans, le 1^{er} et 2 Juin 2022. Nous remercions chaleureusement toute l'équipe d'organisation locale : Frédéric Amiard, Ines Abid, Aïcha Azziz, Mathieu Edely et Marc Lamy de la Chapelle. Nous remercions également le CNRS sans qui nos manifestations ne pourraient se tenir.

Les thématiques du GDR *PES* sont centrées notamment autour de la photo-électrochimie, de la commutation *redox* des propriétés photo-physiques de molécules et nanoparticules. Celles du GDR *Plasmonique Active* concernent entre-autre les processus photo- ou électro-induits, en relation avec l'excitation des plasmon de surface. Les points communs entre les deux GDR sont donc forts, comme en témoignent l'ensemble des séminaires proposés. Ils montrent aussi la richesse et la diversité des projets menés à l'échelle nationale au sein des deux GDR.

Bien cordialement,

M. Fabien Miomandre, directeur du GDR *Photo-Electro-Stimulation*

M. Nordin Félidj, directeur du GDR *Plasmonique Active*

Comment venir à l'Université

Le lieu de conférence est la scène de **EVE**, l'Espace de Vie Etudiante (Avenue René Laennec, 72100 Le Mans)



Site web de EVE : <http://eve.univ-lemans.fr/fr/index.html>

Le plus simple si vous venez de la gare ou du centre ville est de prendre la **ligne T1** du Tramway - **direction Université - Arrêt Campus Ribay** (avant dernier arrêt de la ligne).

Pour utiliser le tramway, vous pouvez acheter les tickets aux machines automatiques situées aux arrêts de tramway.

Site web: <http://www.setram.fr/index.php>

Tarifs

- Ticket unité (validité d'1 heure après validation) : 1,50 euros.
- Ticket aller-retour (validité d'1 heure pour chaque trajet après validation) : 2,90 euros.
- Ticket journée (validité de 24 heures) : 4,20 euros.
- Ticket 10 voyages (validité d'1 heure après chaque validation) : 13,50 euros

Programme des conférences orales

Mercredi 1^{er} Juin 2022

- **10h00-10h30** : Accueil et inscription des participants (autour de cafés et croissants).
- **10h30-10h45** : Introduction des journées par les directeurs des GDR.
- **10h45-11h30** : **Conférence invitée** Jean-Christophe Lacroix, ITODYS, Université Paris Cité, *Plasmonic phenomena in electrochemistry and in molecular electronics: a critical point of view*.
- **11h30-11h50** : Vitor Brasiliense, PPSM, ENS Paris-Saclay, *Dynamically Tracking Surface Modification with Quantitative Phase Imaging*.
- **11h50-12h10** : Agnès Maitre, INSP, Sorbonne Université, *Giant increase of absorption cross section of single nanocrystal within a plasmonic antenna*.
- **12h10-12h30** : Céline Molinaro, IS2M, Université de Haute-Alsace, *Polymerization induced by heat generation through the plasmonic excitation of gold nanoparticles*.

Pause-déjeuner

- **14h00-14h45** : **Conférence invitée** Fabrice Charra, SPEC, CEA, Université Paris Saclay, *Photonic properties of graphene-based 2D supramolecular self-assembled architectures*.
- **14h45-15h05** : Stéphane Rigaut, ISCR, Université de Rennes I, *Photo-Control of NIR Emission*.
- **15h05-15h25** : Ines Abid, IMMM, Université du Mans, *Relation propriétés optiques/propriétés thermiques de nanostructures métalliques*.

Pause-café

- **16h00-16h20** : Nadia Djaker, CSPBAT, Université Paris 13, *Scattering Correlation Spectroscopy based Nanobiosensor: Application for Cu-Zn Superoxyde Dismutase Detection*.
- **16h20-16h40** : Amine Khitous, IS2M, Université de Haute-Alsace, *Synthesis of hybrid nanosensors based on molecularly imprinted polymer by optical near field photopolymerization*.
- **16h40- 17h00** : Laureen Moreaud, SPEC, CEA, Université Paris Saclay, *Gold shell enhancement of dielectric particles as sensitive labels for biological imaging*.
- **17h00-17h20** : Charlène Brissaud, ITODYS, Université Paris Cité, *Plasmonic Photocatalysis: Relative importance of thermal effects and photogenerated reactive oxygen species in aqueous solutions*.
- **17h20-17h30** : Intervention de Jean-Christophe Lacroix : Veille scientifique GDR / Division Nanosciences de la société chimique de France (SCF).
- **17h30** : Session Poster – Buffet

Jeudi 2 Juin 2022

- **9h00-9h45** : *Conférence invitée* Galina Dubacheva, DCM, Univ. Grenoble Alpes, *Reversible fluorescence switching at nano-scale using stimuli-responsive supramolecular interactions*.

- **9h45-10h05** : Guillaume Laurent, PPSM, ENS Paris-Saclay, *Patterning gold nanorod assemblies by deep-UV lithography*.

- **10h05-10h25** : Liudmila Trotsiuk, UTT, Troyes, *Emission of quantum dots near gold nanoparticles: classical plasmonic enhancement and beyond*.

Pause-café

- **11h00-11h45** : *Conférence invitée* Mona Tréguer-Delapierre, ICMCB, Université de Bordeaux, *Synthesis and optical properties of coupled plasmonic nanoparticles: recent advances and perspectives*.

- **11h45-12h05** : Bruno Palpant, LuMIn, CentraleSupélec-ENS Paris-Saclay, *Gold-silver core-shell nanoparticles: Near-ultraviolet plasmon modes and sub-THz vibrations*

- **12h05-12h25** : Théo Geronimi-Jourdain, ITODYS, Université Paris Cité, *Plasmon-mediated surface grafting as an innovative strategy for a direct visualization of surface lattice plasmon modes*

- **12h25- 12h45** : Conclusions des journées GDR.

CONFERENCES ORALES

Plasmonic phenomena in electrochemistry and in molecular electronics: a critical point of view.

Jean-Christophe Lacroix, Mathieu Bastide, Pierre Bleteau,
Sarrah Gam-Derouich

Université de Paris, ITODYS, CNRS-UMR 7086, 15 rue J-A de Baïf, 75205 Paris Cedex 13,
France.

lacroix@univ-paris-diderot.fr

Metallic nanostructures allow the confinement of light on a subwavelength scale due to the collective oscillations of the quasi-free electrons generated at the metal-dielectric interface when irradiated. This phenomenon leads to a strong absorption in the visible or near infra-red range, called localized surface plasmon resonance (LSPR). Electron oscillations cause the creation of hot charge carriers¹ with energies corresponding to typical molecular excitations. As a consequence, their transfer can induce new chemistry in the vicinity of nanoparticles (NPs) and they can be used to achieve chemical, photochemical electrochemical reactions with molecules absorbed on or close to the NPs²⁻⁵. They can also be used in molecular electronics.^{6,7}

In this conference, I will present few phenomena in which hot electron generated by plasmonic nanostructures can be used in electrochemistry and molecular electronics. I will first discuss, the enhancement of electrochemical reductions or oxidations of soluble redox probes in a scanning electrochemical configuration. In a second part, I will show that redox active nanojunction made of conductive polymers can be switched by plasmon induced electrochemical process.^{8,9}

Finally, I will show that diazonium reduction of various molecules can be performed on plasmonic electrodes¹⁰⁻¹⁴ and makes it possible connect gold dimers¹⁵ or to grow lines, columns but also lines and columns of NPs connected by the organic semiconductor, can be generated using NPs of various sizes.¹⁶

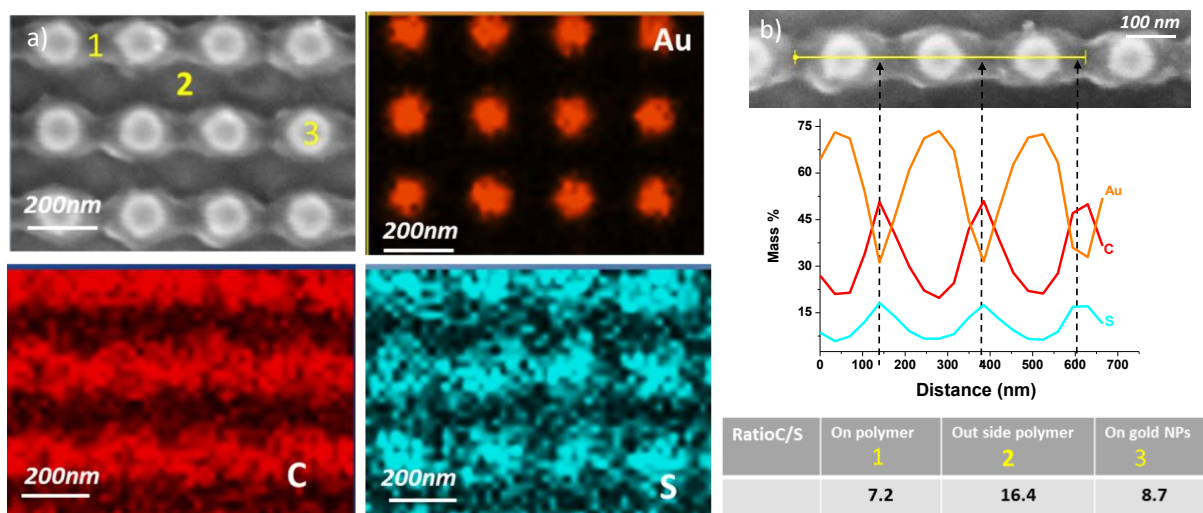


Figure 1: Anisotropic growth of BTB layer on arrays of AuNPs deposited on ITO (diameter 100 nm, gratings $\Lambda_x = \Lambda_y = 200$ nm) after irradiating a 3 mM BTAB solution containing 30 eq. of tBuNO₂ with polarized white light along the x axis of the arrays for 20 min. a) SEM image, gold, carbon and sulfur EDX signals. b) Line profile showing the mass % of gold, carbon and sulfur along one line of NPs connected by oligo(BTB).

Reference

- (1) Manjavacas, A.; Liu, J. G.; Kulkarni, V.; Nordlander, P. Plasmon-Induced Hot Carriers in Metallic Nanoparticles. *ACS Nano* **2014**, *8* (8), 7630–7638.
- (2) Xie, W.; Schlücker, S. Hot Electron-Induced Reduction of Small Molecules on Photorecycling Metal Surfaces. *Nat. Commun.* **2015**, *6* (1), 7570.
- (3) Kim, N. H.; Meinhart, C. D.; Moskovits, M. Plasmon-Mediated Reduction of Aqueous Platinum Ions: The Competing Roles of Field Enhancement and Hot Charge Carriers. *J. Phys. Chem. C* **2016**, *120* (12), 6750–6755.
- (4) Wang, Y.; Wang, S.; Zhang, S.; Scherman, O. A.; Baumberg, J. J.; Ding, T.; Xu, H. Plasmon-Directed Polymerization: Regulating Polymer Growth with Light. *Nano Res.* **2018**, *11* (12), 6384–6390.
- (5) Deeb, C.; Ecoffet, C.; Bachelot, R.; Plain, J.; Bouhelier, A.; Soppera, O. Plasmon-Based Free-Radical Photopolymerization: Effect of Diffusion on Nanolithography Processes. *J. Am. Chem. Soc.* **2011**, *133* (27), 10535–10542.
- (6) Lacroix, J.-C.; van Nguyen, Q.; Ai, Y.; van Nguyen, Q.; Martin, P.; Lacaze, P.-C. From Active Plasmonic Devices to Plasmonic Molecular Electronics. *Polym. Int.* **2019**, *68* (4), 607–619.
- (7) Lacroix, J.-C.; Martin, P.; Lacaze, P.-C. Tailored Surfaces/Assemblies for Molecular Plasmonics and Plasmonic Molecular Electronics. *Annu. Rev. Anal. Chem.* **2017**, *10*, 201–224.
- (8) Ai, Y.; Ghilane, J.; Lacroix, J.-C. Approaching the Frontier Between Fiber Devices and Single-Molecule Devices in Redox Gated Junction. *J. Phys. Chem. C* **2015**, *119* (36), 21278–21285.
- (9) Ai, Y.; Nguyen, V. Q.; Ghilane, J.; Lacaze, P.; Lacroix, J.-C. Plasmon-Induced Conductance Switching of an Electroactive Conjugated Polymer Nanojunction. *ACS Appl. Mater. Interfaces* **2017**, *9* (33), 27817–27824.
- (10) Nguyen, V. Q.; Ai, Y.; Martin, P.; Lacroix, J. C. Plasmon-Induced Nanolocalized Reduction of Diazonium Salts. *ACS Omega* **2017**, *2* (5), 1947–1955.
- (11) Nguyen, M.; Kherbouche, I.; Gam-Derouich, S.; Ragheb, I.; Lau-Truong, S.; Lamouri, A.; Lévi, G.; Aubard, J.; Decorse, P.; Féridj, N.; et al. Regioselective Surface Functionalization of Lithographically Designed Gold Nanorods by Plasmon-Mediated Reduction of Aryl Diazonium Salts. *Chem. Commun.* **2017**, *53* (82), 11364–11367.
- (12) Tijunelyte, I.; Kherbouche, I.; Gam-Derouich, S.; Nguyen, M.; Lidgi-Guigui, N.; de la Chapelle, M. L.; Lamouri, A.; Lévi, G.; Aubard, J.; Chevillat-Biraud, A.; et al. Multi-Functionalization of Lithographically Designed Gold Nanodisks by Plasmon-Mediated Reduction of Aryl Diazonium Salts. *Nanoscale Horizons* **2018**, *3* (1), 53–57.
- (13) Bastide, M.; Frath, D.; Gam-Derouich, S.; Lacroix, J.-C. Electrochemical and Plasmon-Induced Grafting of n-Dopable π -Conjugated Oligomers. *ChemElectroChem* **2021**, *8* (13), 2512–2518.
- (14) Nguyen, L.-L.; Le, Q.-H.; Pham, V.-N.; Bastide, M.; Gam-Derouich, S.; Nguyen, V.-Q.; Lacroix, J.-C. Confinement Effect of Plasmon for the Fabrication of Interconnected AuNPs through the Reduction of Diazonium Salts. *Nanomaterials* **2021**, *11* (8).
- (15) Bléteau, P.; Bastide, M.; Gam-Derouich, S.; Martin, P.; Bonnet, R.; Lacroix, J.-C. Plasmon-Induced Grafting in the Gap of Gold Nanoparticle Dimers for Plasmonic Molecular Junctions. *ACS Appl. Nano Mater.* **2020**, *3* (8), 7789–7794.
- (16) Bastide, M.; Gam-Derouich, S.; Lacroix, J.-C. Long-Range Plasmon-Induced Anisotropic Growth of an Organic Semiconductor between Isotropic Gold Nanoparticles. *Nano Lett.* **2022**.

Dynamically Tracking Surface Modification with Quantitative Phase Imaging

Baptiste Maillot¹, Jean-Frédéric Audibert¹, Tengfei Wu², Gilles Tessier², Fabien Miomandre¹, Pascal Berto², Vitor Brasiliense^{*1}

¹PPSM, CNRS (UMR 5831) ENS Paris-Saclay, 4 avenue des sciences, Gif-sur-Yvette 91190,

² Sorbonne Université, INSERM, CNRS, Institut de la Vision, Paris F-75012, France

E-mail:

vitor.brasiliense@ens-paris-saclay.fr

Grafting of chemical groups onto surfaces is a promising strategy for preparing functional materials, especially when associated with local modification

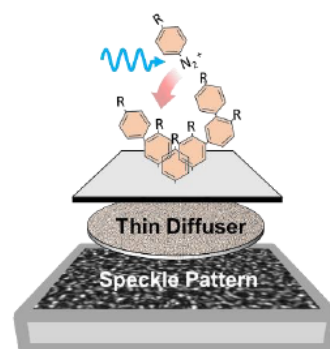
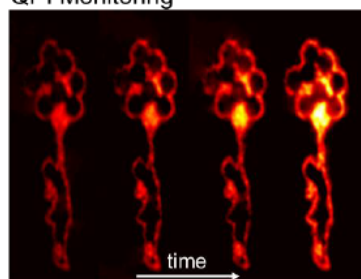
methods. Direct optical photografting of diazonium salts offers a wide scope of functional groups and high (diffraction limited) spatial resolution. However, the reactive nature of the radicals associated with kinetic effects due to substituents often leads to kinetics which are complex and difficult to control, posing a limit to the precision which can be achieved.

In this communication, we present an all-optical strategy to mitigate this difficulty, using quantitative phase imaging (QPI) methods to carefully, accurately and non-invasively track the advancement of the surface modification reaction^[1]. Using DIPSI, an inexpensive quantitative phase imaging technique^[2], we show that the photografting of several diazonium salts can be tracked from its onset until several hundreds of nanometers with subnanometric precision. We demonstrate potential applications of the strategy by analyzing the effect of substituents on the photografting kinetics, by designing complex patterns onto glass slides and analyzing in a quantitative manner the role of sensitizers and catalysts.

References

- [1] Brasiliense, V., Audibert, J.-F., Wu, T., Tessier, G., Berto, P., Miomandre, F., Local Surface Chemistry Dynamically Monitored by Quantitative Phase Microscopy. *Small Methods*, 6, 2100737 (2022).
- [2] Berto, P., Rigneault, H., Guillon, M., Wavefront sensing with a thin diffuser, *Opt. Lett.* 42, 5117-5120 (2017).

QPI Monitoring



Giant increase of absorption cross section of single nanocrystal within a plasmonic antenna

A. R. Dhawan¹, M. Nasilowski³, B. Dubertret³, A. Maître¹

¹*Institut des NanoSciences de Paris, Sorbonne Université, Paris.*

²*Laboration de physique et d'étude des Matériaux, ESPCI, Paris*

E-mail : agnes.maitre@insp.upmc.fr

Nanometric semi-conductor colloidal nanocrystals, like CdSe/CdS ones, are excellent single photon sources. Their emission is stable and bright, with a spectral bandwidth of the order of $\Delta\lambda=20\text{-}30\text{nm}$. In specific conditions of high excitation or high confinement, their emission is dramatically changed. They lose their single photon source quality, the dynamic of the emission is accelerated. the spectrum becomes very large and can reach a few 100nm. Such condition can be achieved either by exciting at high power the emitters or by coupling them to antennas [1], increasing optical confinement.

By in situ optical lithography using high order Laguerre Gaussian mode, we deterministically positioned a single colloidal CdSe/CdS emitter inside a plasmonic patch antenna. The single nanocrystal embedded in a thin dielectric medium, is sandwiched between a thick gold layer and thin gold patch. We achieve inside plasmonic antennas a high interaction between the emitters and the confined field excited inside the antenna. We observe large modification of emission for quantum inside antennas illustrated by directive emission, high brightness and increased

efficiency. We evidence a dramatic increase of absorption cross-section of emitters inside these antennas. At higher excitation, multi excitation recombination becomes radiative and the emission intensity becomes non linear [2].

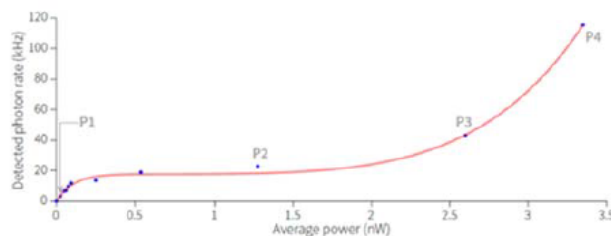


Fig 1: Emission of the antenna with increasing excitation power

References

- [1] A. R. Dhawan, C. Belacel, J. U. Esparza-Villa, M. Nasilowski, Z. Wang, C. Schwob, J.-P. Hugonin, L. Coolen, B. Dubertret, P. Senellart, A. Maître, *Light: Science and applications*, **9**, 33 (2020)
- [2] A. R. Dhawan, M. Nasilowski, Z. Wang, B. Dubertret, A. Maître, *Advanced materials* **34**, 2108120 (2022)

Polymerization induced by heat generation through the plasmonic excitation of gold nanoparticles

C. Molinaro,^{1,2} A. Khitous,^{1,2} F. Kameche^{1,2} and O. Soppera

¹Université de Haute Alsace, CNRS, IS2M UMR 7361, 68100, Mulhouse, France

²Université de Strasbourg, 67000, Strasbourg, France

E-mail: celine.molinaro@uha.fr

Localized surface plasmon-induced polymerization of free-radical acrylate monomers is an efficient, smart, and versatile method for preparing metal/polymer hybrid nanoparticles (NPs) with accurate control of the thickness and spatial distribution of the polymer on the NP surface. Despite a growing number of practical demonstrations, the mechanism leading to polymerization of the acrylate monomer by localized surface plasmon resonance is still controversial. Indeed, through decay processes, the plasmon emitted light, hot charge carriers and heat (Figure 1). If these processes are well-known, the main difficulty is to discriminate between them.

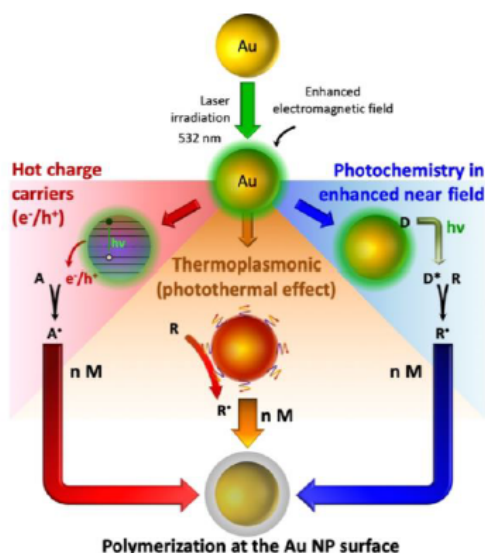


Figure 1: Schematic of the three main pathways to graft polymer through the plasmonic excitation of gold NPs [1].

Previous experiments performed in the laboratory, highlighted the photochemical pathway as the main mechanism under mild irradiation [1]. The thermoplasmonic pathway was already used to cure InZnO thin films [2]. Here, we investigated thermoplasmonic to graft thermopolymer onto NPs. Different parameters are considered to address specifically thermopolymerization through the plasmonic excitation of NPs (i.e. single/assembly of NPs, continuous/pulsed laser excitation...).

References

- [1] F. Kameche et al., J. Phys.Chem.C.,128, 8719-8731 (2021)
- [2] C-F. Lin et al., Adv. Opt. Mater., 2100045 (2021)

Photonic properties of graphene-based 2D supramolecular self-assembled architectures

Fabrice Charra,

SPEC, CEA/CNRS, UMR 3680, Université Paris-Saclay, France (fabrice.charra@cea.fr)

Designing van der Waals (vdW) heterostructures based on two-dimensional (2D) materials is blossoming as a promising route to the fabrication of new materials with electronic and photonic responses tailored at the nanoscale. A strong limitation results from the limited choice of easily processible 2D materials with complementary properties, beyond the sole graphene. However, graphene properties can be tuned through its functionalization by specific active photonic molecules. We have recently developed original molecular-engineering concepts for designing molecular building blocks spontaneously adsorbing on graphene according to various preprogrammed patterns.[1] We shown that such “augmented graphene” layers can be stacked on each other to form original vdW heterostructures.[2] We have realized and probed the photonic responses of such single or bi-layer structures embedding one or several molecular or polymeric building blocks. The STM images permit an accurate structural analysis of molecular organization induced by the atomic-scale template of graphene. The organized self-assembly has a clear influence on optical properties, as observed by absorbance,[3,4] fluorescence[5] and Raman micro-spectroscopy. These experiments permit to distinguish the influence on optical spectra of the various molecule-molecule and molecule-graphene interactions of either electronic or near-field optical origins. The possibility of assembling different molecules with perpendicularly-oriented transition dipole moments (see figure) opens new perspectives towards hyperbolic metamaterials.

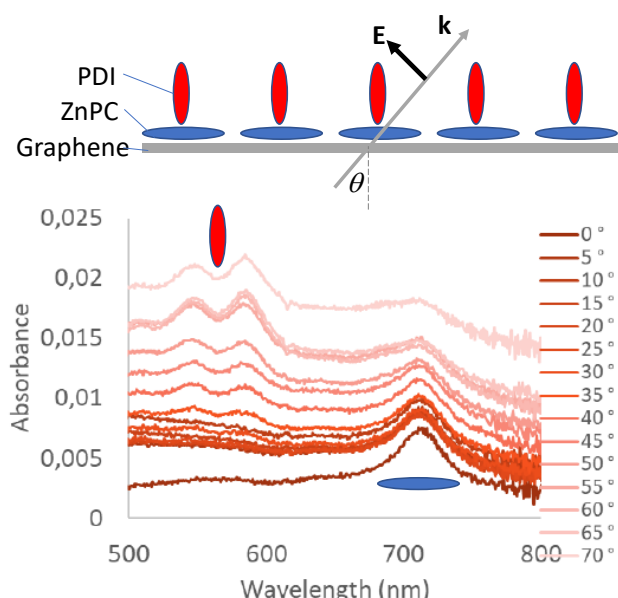


Figure: Incidence-angle resolved absorption of an organized monolayer of in-plane Zinc Phthalocyanine derivatives (absorption peak at 710nm) and out-of-plane perylene derivatives (540-600nm) formed by self-assembly onto a graphene.

- [1] N. Kalashnyk et al, Chem. Commun.54, 9607-9610 (2018)
- [2] N. Kalashnyk et al, 2D Mater. 6, 045016 (2019)
- [3] T. Sghaier et al, Beilstein J. Nanotechnol. 7, 862-868 (2016)
- [4] S. Le Liepvre et al, Mol. Cryst. Liq. Cryst. 65, 5-15 (2017)
- [5] S. Le Liepvre et al, ACS Photonics 3, 2291-2296 (2016)

Photo-Control of NIR Emission

Hassan Al Sabea,¹ Lucie Norel,¹ Olivier Galangau,¹ Olivier Maury,²
François Riobé,² and Stéphane Rigaut¹

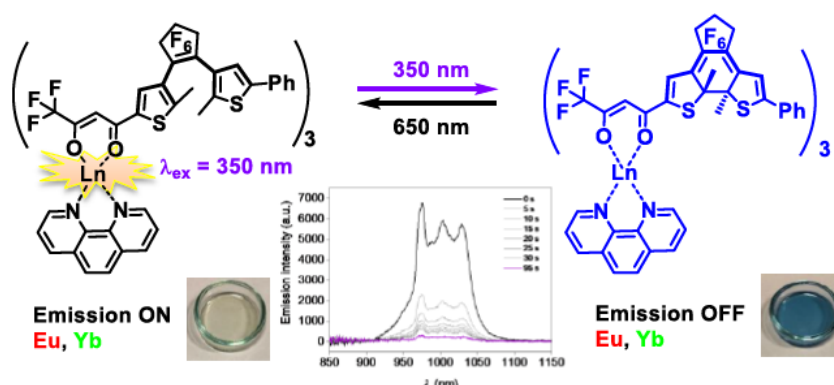
¹ Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes UMR 6226, F-35000 Rennes, France

²Univ. Lyon, CNRS, ENS Lyon, Laboratoire de Chimie UMR 5182 46 allée d'Italie, F-69007 Lyon, France

stephane.rigaut@univ-rennes1.fr

Lanthanide ion complexes display unique long-lived and narrow bandwidth luminescence ranging from the visible up to the near infra-red spectral ranges. Hence, they led to wide applications in material chemistry and biological imaging. Remote control of this luminescence is now an attractive target for the development of more elaborated optical materials.

For this purpose, our group recently focused on the development of photochromic lanthanide complexes, with a special interest in the NIR emitting ytterbium(III) ion since it is much less studied than the red emitting europium(III) ion. In particular, we achieved a photochromic β -diketonate ligand having a dithienylethene unit that is very efficient for the switching ON and OFF of ytterbium(III) luminescence. This system presents a dynamic response which behavior can be transferred to polymer films. We also developed a complex having an additional antenna allowing non-destructive read-out and redox-switching.



References

- [1] L. Norel, O. Galangau, H. Al Sabea, S. Rigaut, *ChemPhotoChem* **2021**, 5, 393-405
- [2] H. Al Sabea, L. Norel, O. Galangau, T. Roisnel, O. Maury, F. Riobé, S. Rigaut, *Adv. Funct. Mater.* **2020**, 30, 2002943
- [3] H. Al Sabea, L. Norel, O. Galangau, H. Hijazi, R. Métivier, T. Roisnel, O. Maury, C. Bucher, F. Riobé, S. Rigaut, *J. Am. Chem. Soc.* **2019**, 141, 20026-20030

Relation propriétés optiques/propriétés thermiques de nanostructures métalliques

Abid Inès¹, Christophe Naveaux¹, Andreea Campu², Monica Focsan², Mathieu Edely¹, Marc Lamy de La Chapelle¹

¹*Institut des Molécules et Matériaux du Mans (IMMM - UMR CNRS 6283), Université du Mans, Avenue Olivier Messiaen, 72085 Le Mans CEDEX 9*

²*Nanobiophotonics Laboratory, Institute for Interdisciplinary Experimental Research in Bionanoscience, Treboniu Laurian 42, Cluj-Napoca, Romania*

E-mail: ines.abid@univ-lemans.fr

Grâce à leurs résonances plasmoniques, les nanostructures métalliques confinent l'énergie lumineuse à l'échelle nanométrique, ils se comportent donc comme des nanosources optiques. Cette énergie est ensuite relaxée dans la nanoparticule sous forme de chaleur et ces résonateurs se transforment alors en nanosources de chaleur [1]. Ainsi, via le contrôle des propriétés optiques de la nanoparticule facilement modulables, il est possible de contrôler la température à l'échelle nanométrique.

Dans ce cadre nous nous sommes intéressés à l'étude de la relation propriétés optiques/ propriétés thermiques des nanostructures plasmoniques. A l'aide d'une caméra thermique et d'un laser pulsé accordable, nous avons pu mesurer l'élévation de la température d'une solution de nanoparticules d'Au dans l'eau, en fonction de la longueur d'onde d'excitation. Nous avons mis en évidence une augmentation de la température de la solution, directement liée à l'absorption plasmonique pour des particules d'Au de 50 nm. Pour des particules de plus grande taille, un échauffement de la solution lié plutôt à la diffusion optique a été démontré.

L'effet de la forme des particules sur ce phénomène d'hyperthermie a été également étudié. Nous avons observé une meilleure efficacité en terme de dégagement de chaleur pour des particules bipyramidales par rapport aux particules sphériques, pour des concentrations équivalentes.

Nous avons aussi montré que l'échauffement de la solution est linéairement proportionnel à la concentration en particules et à la densité optique d'excitation.

Ces résultats contribuent à une meilleure compréhension du transfert thermique entre les nanostructures plasmoniques et leur milieu environnant, dont le contrôle est la clé pour plusieurs applications comme le traitement du cancer par hyperthermie [2], le transfert in vivo de médicaments [3], et la thermophotovoltaïque [4].

References

- [1] Baffou, G. and Quidant, R., 7, 171-187 (2013)
- [2] Nardine S. Abadeer et Catherine J. Murphy, 120, 4691–4716 (2016)
- [3] Pan, L., Bogoy, D, 3, 189–190 (2009)
- [4] Pillai et M.A. Green, 94, 1481–1486 (2010)

Scattering Correlation Spectroscopy based Nanobiosensor: Application for Cu-Zn Superoxyde Dismutase Detection

R. Dekhili,¹ M. Chalal,¹ Q. Liu,¹ M. Lamy de la Chapelle,² J. Spadavecchia¹ and N. Djaker¹

¹Université Sorbonne Paris Nord, UFR SMBH, Laboratoire CSPBAT, CNRS (UMR 7244), 74 rue Marcel Cachin, F-93017 Bobigny, France

²Institut des Molécules et Matériaux du Mans (IMMM - UMR CNRS 6283), Université du Mans, Avenue Olivier Messiaen, 72085 Le Mans, France

E-mail: nadia.djaker@univ-paris13.fr

Gold nanoparticles (GNP) possess exceptional physico-chemical properties, which allow their use in many biomedical fields, such as drug delivery and photothermal therapy. [1] Generally, GNP properties depend on the synthetic procedure used to produce them and the subsequent surface chemistry, which affects directly their geometrical properties such as shape and size. [2, 3] The main techniques used for proteins-GNP interaction characterization are surface plasmon resonance (SPR) [4] or surface enhanced Raman spectroscopy. [5] Recently, more sensitive techniques based on the measurement of the hydrodynamic radius of the nanoparticles before and after interaction with proteins in a very small detection were developed. As compared to conventional techniques, SCS is more sensitive for size measurements. In the case of protein-GNP interaction, we have demonstrated that SCS is a powerful tool to explore the plasmatic proteins adsorption on GNP, by monitoring the changes in the Brownian diffusion due to the protein binding. [6] Using the same methodology, we will show you in this presentation a new type of nano-biosensors based on SCS for SOD proteins family detection.

References

- [1] W.Z. Song, J.X. Gong, Y.Q. Wang, Y. Zhang, H.M. Zhang, W.H. Zhang, H. Zhang, X. Liu, T.F. Zhang, W.Z. Yin, W.S. Yang, J. Nanoparticle Res., 18 (2016).
- [2] G. Marguerit, H. Moustauoui, M. Ben Haddada, N. Djaker, M.L. de la Chapelle, J. Spadavecchia, Part. Part. Syst. Charact., 35 (2018).
- [3] H. Moustauoui, D. Movia, N. Dupont, N. Bouchemal, S. Casale, N. Djaker, P. Savarin, A. Prina-Mello, M.L. de la Chapelle, J. Spadavecchia, ACS Appl. Mater. Interfaces, 8 (2016).
- [4] T. Cedervall, I. Lynch, S. Lindman, T. Berggard, E. Thulin, H. Nilsson, K.A. Dawson, S. Linse, Proc. Natl. Acad. Sci. USA, 104 (2007).
- [5] P.D. Howes, R. Chandrawati, M.M. Stevens, Science, 346 (2014).
- [6] H. Moustauoui, J. Saber, I. Djeddi, Q.Q. Liu, D. Movia, A. Prina-Mello, J. Spadavecchia, M.L. de la Chapelle, N. Djaker, Nanoscale, 11 (2019).

Synthesis of hybrid nanosensors based on molecularly imprinted polymer by optical near field photopolymerization

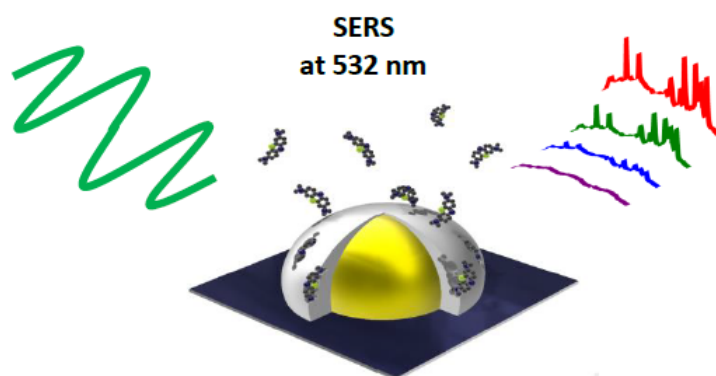
Amine Khitous^{1, 2}, Céline Molinaro^{1, 2}, Simon Gree^{1, 2}, Karsten Haupt³, Olivier Soppera^{1, 2}

¹ Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

² Université de Strasbourg, France

³ Université de Technologie de Compiègne, France
E-mail: olivier.soppera@uha.fr

A new simple, fast and versatile method for the functionalization of gold nanoparticles (AuNPs) by a nanoscale layer of molecularly imprinted polymers (MIPs) was developed. The key step is based on near-field radical photopolymerization of a MIP pre-polymerization mixture. This allows the preparation of hybrid AuNPs@MIPs nanoparticles which are used as substrates for LSPR and surface enhanced Raman spectrometry (SERS) analyses with excellent sensitivity and specificity. To demonstrate the performance of AuNPs@MIPs, MIPs specific to methylene blue (MB) were prepared. The sensitivity of spectroscopic detection is in the range of 10 nM. Specificity is demonstrated by comparing the response with a control non-printed polymer (NIP) and by interference tests with two analogues (Rhodamine 6G and Rhodamine 110). This fabrication method allowed us to obtain robust and recyclable sensing surfaces with high sensitivity and selectivity. The nanometric thickness of MIP allows a short analysis time (10 min), which improves the performance of MIP-based sensors and opens new perspectives to detect molecules at very low concentrations.



References:

- [1] Khitous, A et al, in preparation
- [2] Kameche, F et al, The Journal of Physical Chemistry C **2021**, 125 (16), 8719–8731.
- [3] Paruli, E et al, ACS Applied Polymer Materials **2021**, 3 (10), 4769–4790.

Gold shell enhancement of dielectric particles as sensitive labels for biological imaging

L. Moreaud¹, G. Boudan¹, A. Loirette-Pelous⁵, A. Bogicevic², J.-J. Greffet⁵, T. Pons², C. Bogicevic³, F. Marquier⁴, S. Vassant¹, and C. Fiorini¹

¹SPEC, CEA, Université Paris Saclay, CNRS, Gif-sur-Yvette, France

²LPEM, ESPCI Paris, Université Paris Saclay, CNRS, Paris, France

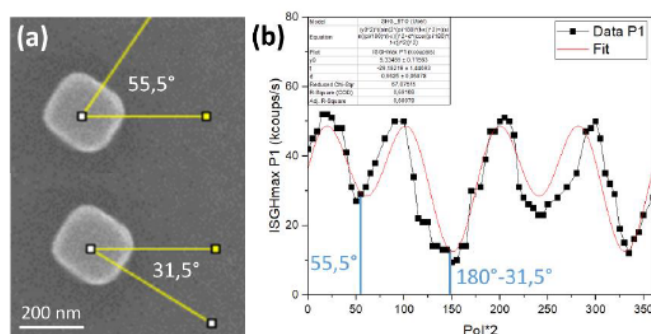
³SPMS, CentraleSupélec, Université Paris-Saclay, CNRS, Gif-sur-Yvette, France

⁴LuMIn, ENS Paris-Saclay, Université Paris-Saclay, CNRS, Gif-sur-Yvette, France

⁵LCF, IOGS, Université Paris-Saclay, CNRS, Palaiseau, France

E-mail: Laureen.moreaud@cea.fr

A decade ago, observations of abnormalities in intraneuronal transport by molecular motors of biomolecules have been identified as a functional readout of Alzheimer's condition.[1] Currently, fluorescence microscopy is an excellent tool to probe the intraneuronal transport of endosomes labeled with a fluorophore.[2] However, this technique usually doesn't address the rotational dynamics. On the contrary, the second harmonic generation (SHG) signal depends on the polarization of the excitation field and thus gives information about the particle orientation. By crossing SEM images and SHG measurements, we demonstrate the correlation between the SHG anisotropy measurements of monocrystalline barium titanate particles (BTO) and their orientation. Moreover, BTO particles coated with 10 nm of gold are considered to study the possibility of enhancing the SHG signal to ensure a good marking sensitivity, particularly in the case of small particles. Yet, the first measurements revealed only a factor 2 enhancement of the SHG intensity, which appears much less than previously reported in the literature [3]. We will evidence that specific care is crucial to avoid laser-induced reshaping of the gold coating. Furthermore, we show that the laser excitation wavelength needs to be accurately optimized to maximize the SHG enhancement.



(a) SEM images of a BTO particle indicating its orientation on the substrate. (b) SHG intensity dependence with the incident laser polarization. Experimental data are consistent with the theoretical responses expected from the BTO orientations shown in (a).

References

- [1] Stokin et al., Science 307, 1282–8 (2005).
- [2] Haziza et al., Nat. Nanotechnol. 12, 322–328 (2017).
- [3] Pu et al., PRL 104, 207402 (2010).

Plasmonic Photocatalysis: Relative Importance of Thermal Effects and Photogenerated ROS in Aqueous Solutions

Charlène Brissaud¹, Yoel Negrín-Montecelo,^{2,3} Lucas V. Besteiro,^{2,3} Jean-Yves Piquemal,¹ Alexander O. Govorov,⁴ Miguel A. Correa-Duarte^{2,3} and Miguel Comesaña-Hermo¹

¹Université Paris Cité, ITODYS, CNRS, UMR 7086, 15 rue J-A de Baïf, F-75013 Paris, France

²CINBIO, Universidade de Vigo, Department of Physical Chemistry, 36310 Vigo, Spain

³Galicía Sur Health Research Institute (IISGS), CIBERSAM, 36310 Vigo, Spain

⁴Department of Physics and Astronomy, Ohio University, Athens, 45701 Ohio, United States

E-mail: charlene.brissaud@etu.u-paris.fr

Synergic combination of plasmonic metals and large bandgap semiconductors such as TiO₂ has been widely used to form broadband photocatalysts with enhanced activities and efficiencies into the visible and near-infrared regions of the electromagnetic spectrum.¹ The efficiency of the plasmonic photosensitization process depends on three main effects: the generation of excited charge carriers, the local enhancement of the electromagnetic field at the surface of the plasmonic nanoparticles and the photogeneration of heat. Therefore, separating the relative importance of thermal and non-thermal features upon plasmonic excitation is essential to better understand the mechanisms behind plasmon-induced photocatalysis.²

To this aim, we have used a colloidal Au-TiO₂ hybrid as photocatalyst for the plasmonic photo-oxidation of a model organic substrate in aqueous solution. Experimental procedures supported by simulations allow us to separate the role played by the excited charge carriers from thermal dissipation in the photocatalytic process. Moreover, the interaction of photogenerated charge carriers with H₂O and O₂ leads to the formation of reactive oxygen species (ROS) that play an important role in photo-oxidation reactions.³ Their identification can supply relevant information on the reactivity of the photogenerated hot electrons and hot holes in the photocatalyst.

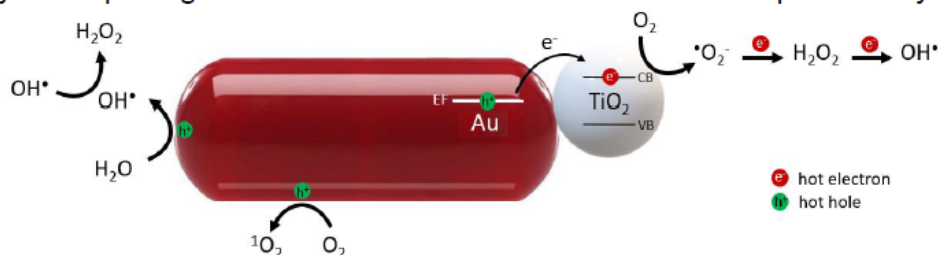


Figure 1. Schematic representation of the formation of different ROS on Au-TiO₂ photocatalyst.

References

- [1] Linic, S. et al. *Nat. Mater.* **2011**, *10*, 911–921.
- [2] Baffou, G. et al. *Light Sci. Appl.* **2020**, *9*, 108.
- [3] Sousa-Castillo, A. et al. *J. Phys. Chem. C* **2016**, *120*, 11690–11699.

Reversible fluorescence switching at nano-scale using stimuli-responsive supramolecular interactions

B. Chabaud,^a F. Sciortino,^a L. Martin,^a D. Kamzabek,^b H. Bonnet,^a R. Lartia,^a F. Miomandre,^b R. Auzély,^c L. Guérente,^a D. Boturyn,^a and **G. V. Dubacheva^a**

^aDCM, Univ. Grenoble Alpes; ^bPPSM, ENS Paris-Saclay; ^cCERMAV, Grenoble

Email: galina.dubacheva@univ-grenoble-alpes.fr

Tuning fluorescence reversibly and in a single nanostructure is of great interest for the development of bioanalytic nanoprobe, sensing and photo-electronic devices. We propose to use stimuli-responsive supramolecular interactions to design dynamic plasmonic systems allowing reversible fluorescence switching by tuning the nanoparticle/fluorophore distance. Our recent results obtained with gold nanoparticles linked with fluorescein through thermoresponsive poly(N-isopropylacrylamide) provided the proof for the proposed approach (Fig. 1A) [1]. We are now extending it to oligo(ethylene glycol) copolymers having tunable transition temperature, aiming to produce multifunctional nano-probes, combining the possibility of local heating with nano-scale temperature sensing. In parallel, we develop fluorescence switches based on redox-driven host/guest interactions such as between β -cyclodextrin and its guest ferrocene (Fig. 1B). Our previous studies on surfaces revealed several advantages of host/guest chemistry for the controlled surface binding such as strong and specific interactions combined with reversibility under external stimuli [2-4]. Our goal is to extend this strategy from surfaces to nanostructures by developing redox- or photosensitive nano-switches suitable for fluorescence sensing assays in solutions and on surfaces.

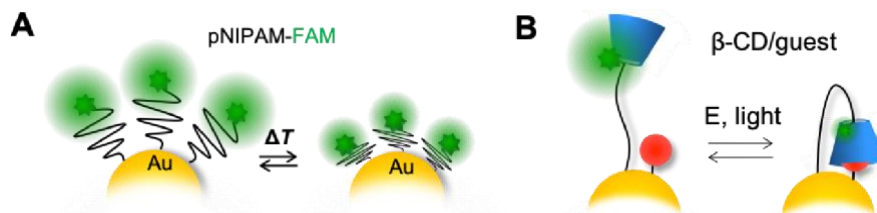


Fig. 1. Fluorescence nano-switches based on thermo-responsive polymers (A) and host/guest interactions sensitive to electrochemical stimuli or light (B).

[1] D. Kamzabek et al, *Langmuir*, 37, 10971–10978 (2021)

[2] G. Dubacheva et al., *Langmuir*, 26, 13976-13986 (2010)

[3] G. Dubacheva et al., *Chem. Commun.*, 47, 3565-3567 (2011)

[4] G. Dubacheva et al., *Proc. Natl. Acad. Sci. USA*, 112, 5579-5584 (2015)

Patterning gold nanorod assemblies by deep-UV lithography

C. Jégat¹, E. Rollin², L. Douillard², O. Soppera³, K. Nakatani¹ and G. Laurent¹

¹ Université Paris-Saclay, ENS Paris-Saclay, CNRS UMR 8531, PPSM, 91190 Gif-sur-Yvette, France

² Université Paris-Saclay, CEA SPEC, CNRS UMR 3680, 91190 Gif-sur-Yvette, France

³ Université de Haute Alsace, CNRS, IS2M UMR 7361, 68100, Mulhouse, France
E-mail: guillaume.laurent@ens-paris-saclay.fr

Metallic nanoparticles perform in many fields: photovoltaic, modulation of molecular properties, multimodal imaging, photothermal therapy and biosensing. In order to develop future meta-material applications, nanoparticle assemblies are promising materials. Such goal can only be achieved by controlling at the same time the inter-particle distance (nanoscale) and the large 2D area patterning (microscale).

We present a new method to pattern assemblies of gold nanorods (GNRs) on substrates and a study of the near-field coupling induced by the aggregation of the nanoparticles. Combination of deep-UV lithography [1] and controlled deposition of functionalized GNRs generates complex GNR assemblies. Near-field coupling is investigated by photoemission electron microscopy (PEEM) [2] on single, dimer and elongated aggregates of GNRs. This comparative study exhibits different kinds of near-field coupling efficiency that occur depending of the incident light polarization, interparticle gaps and angles between the nanorods. Hot spots of the near field are associated to the interparticle gap regions.

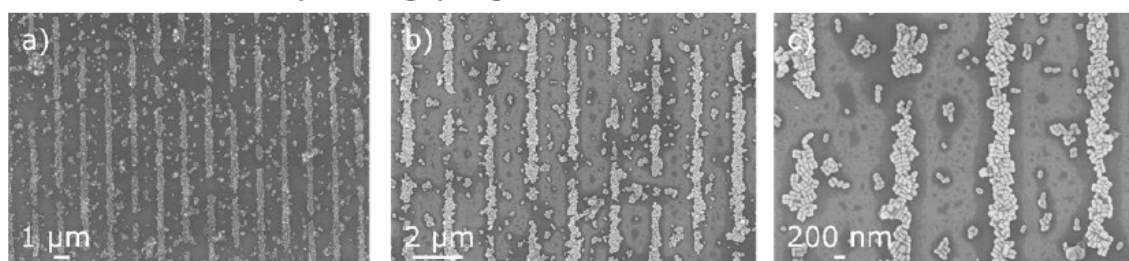


Figure 1. SEM images of gold nanorods selectively deposited on silicon wafer using deep-UV patterning and specific nanoparticles' functionalization.

References

- [1] B. Leuschel; A. Gwiazda; W. Heni; F. Diot; S. Yu; C. Bidaud; L. Vonna; A. Ponche; H. Haidara; O. Soppera, Sci. Rep. 8, 1-15 (2018).
- [2] L. Douillard; F. Charra; C. Fiorini; P. M. Adam; R. Bachelot; S. Kostcheev; G. Lerondel; M. L. De La Chapelle; P. Royer, J. Appl. Phys. 101, 083518 (2007).

Emission of quantum dots near gold nanoparticles: classical plasmonic enhancement and beyond

L. Trotsiuk

¹*University of Technology of Troyes, Troyes, France*

²*B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus*

E-mail: liudmila.tratsiuk@utt.fr

Hybrid plasmon-exciton structures is an extraordinary and powerful tool for the light and charge carriers control at the nanoscale. Precise manipulating of the efficiency, polarizability and chirality of an emission as well as the charge separation and carrier recombination providing by plasmon nanoparticles open emerging possibilities to fabricate advanced optical materials and devices [1]. Among various excitonic structures, quantum dots (QDs) with their tunable, strong and narrow-band emission are especially promising for numerous applications [2] and creation hybrid systems with improved properties.

In this work, we investigated the manipulation of the emission of CdSe/ZnS QDs by gold nanoparticles of various shape. We showed the importance of the control of the QD concentration in complexes with gold nanorods and the specific spectral overlap for the fluorescence enhancement. These allowed achieving one order of magnitude amplification of the emission intensity for QDs with the initial 20% quantum efficiency [3]. Moreover, we investigated the emission behavior of QD attached to gold nanoparticles (nanospheres and nanorods) beyond plasmonic enhancement conditions. We found nearly 4-fold increase in the fluorescence intensity for QDs closely (up to 1.5 nm) adsorbed on the gold nanoparticle surface under the excitation of interband transitions, which we attribute to the possible QD recovering.

References

- [1] J. Schuller et al, *Nature Materials* 9, 193 (2010)
- [2] F.P. García de Arquer, *Science* 373, 640 (2021)
- [3] L. Trotsiuk et al, *Nanotechnology* 31, 105201 (2020)

Synthesis and optical properties of coupled plasmonic nanoparticles: recent advances and perspectives

Mona Tréguer-Delapierre

ICMCB-CNRS, U.Bordeaux, 87 Av du Dr A. Schweitzer, 33608 Pessac

Metallic nanoparticles offer a large of exciting properties, such as intense absorption and scattering, highly efficient light-to-heat conversion and localized field enhancement. As a consequence, they have been used in a wide range of applications in recent years. When group into clusters of specific geometries, they can generate remarkable optical properties such as optical magnetism which has motivated the development of new fabrication techniques. Such clusters could serve as building blocks in a new generation of self-assembled metamaterials (1,2). In this communication, we will describe the geometries, fabrication techniques and optical properties of symmetric clusters of plasmonic particles. We will also present the optical properties of the resonant particles when coupled with thin-films stacks. Disordered ensembles of plasmonic nanoparticles onto such layered films have high potential for mastering visual appearance of an object at the macroscale. The coupling of nanoscale resonances and mesoscale interferences can be used to engineer spectrally and angularly the reflected light and lead to novel visual effects that are particularly impressive when changing viewing conditions.

1.L.Roach, L.Lermusiaux, A.Baron, M.Tréguer-Delapierre in *Encyclopedia of Nanomaterials* edited by Y.Yadong and Y.Xia, (Elsevier, 2021, 1-17, ISBN 978-0-12-822425-0.000011-7)

2.L.Lermusiaux, L.Roach, A.Baron, M.Tréguer-Delapierre, *Nano Express*, 3, 2, 21003 (2022)

3. K. Vynck, R. PAcanowshi, A.Dufay, X. Granier, P.Lalanne, arXiv:2111.13426, (2021)

Gold-silver core-shell nanoparticles: Near-ultraviolet plasmon modes and sub-THz vibrations

T. O. Otomalo^{1,2}, L. Di Mario³, C. Hamon⁴, D. Constantin⁴, F. Toschi³, K.-V. Do¹, V. Juvé², P. Ruello², P. O’Keeffe³, F. Toschi³, D. Catone³, A. Paladini³, and B. Palpant¹

¹ Univ. Paris-Saclay, CNRS, ENS-PS, CentraleSupélec, LuMIn, Gif^s/Yvette, France

² Inst. des Molécules et Matériaux du Mans, CNRS, Le Mans Univ., Le Mans, France

³ Istituto di Struttura della Materia - CNR, EuroFEL Support Lab. (EFSL), Rome, Italy

⁴ Université Paris-Saclay, CNRS, LPS, Orsay, France

E-mail: bruno.palpant@centralesupelec.fr

Irradiating plasmonic nanoparticles (NPs) by ultrashort laser pulses produces a series of transient phenomena that can be exploited in various fields, from targeted therapies to nanoscale broadband radiation sources. These phenomena can be ascribed to the dynamics of the metal hot electron gas induced by multiphoton absorption, which can be monitored by recording the transient evolution of the NP optical response. The plasmon modes of noble metal NPs cover the visible and near-infrared spectral ranges. Although the NP size, shape, and composition influence the characteristics of these modes, it is impossible to access strong resonances in the near-ultraviolet, while this would yet be potentially beneficial for many applications.

In this communication, we study both the stationary and transient optical properties of bimetallic AuNR@Ag nanocuboids consisting of a gold nanorod core (AuNR) coated with a silver shell with variable thickness. Broadband transient absorption spectroscopy was carried out to determine their ultrafast optical dynamics. High-energy transverse modes generate strong and spectrally narrow variations of the NP extinction in the near-UV [1]. In addition, we show that the transient optical response is more sensitive to resonance modes than its stationary counterpart.

Furthermore, analyzing the transient absorption by fast Fourier transform reveals NP vibration modes from 15 to 150 GHz frequency. Simulations allow us to address this vibrational landscape. We demonstrate that the AuNRs@Ag NPs undergo complex motions involving facets, edges, and corners [2].

References

- [1] T. O. Otomalo, L. Di Mario, C. Hamon *et al.*, “Sharp spectral variations of the ultrafast transient light extinction by bimetallic nanoparticles in the near-UV”, *Adv. Opt. Mater.*, **9**, 2001778 (2021).
- [2] T. O. Otomalo, L. Di Mario, C. Hamon, D. Constantin *et al.*, “Acoustic vibration modes of gold-silver core-shell nanoparticles”. *Submitted*.

Plasmon-mediated surface grafting as an innovative strategy for a direct visualization of surface lattice plasmon modes

T. Geronimi-Jourdain¹, M. Braïk², N. Harou¹, A. Belkhir², S. Lau-Truong¹, A. Chevillot-Biraud¹, C. Mangeney³, N. Félidj¹

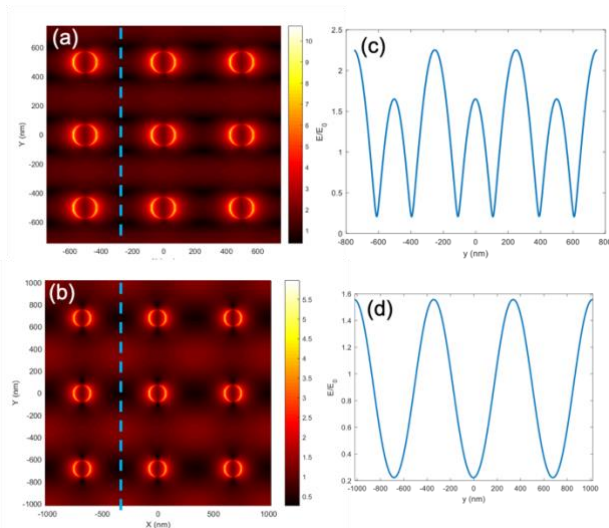
¹ Université Paris Cité, CNRS, ITODYS, F-75006 Paris, France

² Laboratoire de Physique et Chimie Quantique, Université Mouloud Mammeri,
Tizi-Ouzou, Algérie

³ Université Paris Cité, CNRS, LCBPT, F-75006 Paris, France

E-mail: nordin.felidj@u-paris.fr

Plasmonic nanostructures arranged in regular arrays support lattice plasmon modes, thanks to the diffraction of photonic modes of different 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 [1]. Therefore, such arrays can provide improved platforms in the context of non-linear optics, molecular sensing, plasmon-based lasers, or surface enhanced spectroscopies. In this work, we show that the 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 nature of these photonic modes, which is of crucial importance in the understanding of the long-range coupling origin of the plasmonic structures.



Figure(a) and (b): mapping of the intensity of the electric field, obtained by the FDTD method, of two regular arrays of gold disks (diameter 150 nm, height 50 nm, on an ITO layer), for a grating constant of (a) $\Lambda = 500$ nm, and (b) $\Lambda = 680$ nm. The graphs (c) and (d) display the profile of the intensity corresponding to the vertical dashed lines in (a) and (b), respectively. The profile in (c) evidences the photonic mode of the (1,0) order related to the mapping in (a), and the profile in (d), the photonic mode of the (1,1) order related to the mapping in (b).

References

- [1] I. Ragheb *et al.*, J. Opt. Soc. Am. B **36**, E36-E41 (2019)
- [2] I. Kherbouche *et al.*, Nanoscale, **13**, 11051-11057 (2021)

POSTERS

Sensing performances of commercial SERS substrates

A. Azziz¹ W. Safar¹ Y. Xiang² M. Edely¹ M. Lamy de la Chapelle^{1,2}

¹ IMMM - UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans, Cedex 9, France

² Department of Clinical Laboratory Medicine, Southwest Hospital, Third Military Medical University, Chongqing, China

E-mail: Aicha.Azziz.Etu@univ-lemans.fr

Depuis la découverte de la spectroscopie Raman exaltée de surface (SERS) et la capacité de cette technique à détecter des molécules à très faible concentration, de nombreuses techniques ont été réalisées pour fabriquer des substrats qui garantissent un signal SERS fiable et reproductible sur toute leur surface.

Nous avons étudié les performances de détection de trois substrats SERS commerciaux (RAM-SERS-SP de Ocean Optics, QSERS de Nanova Inc. et Hamamatsu de Hamamatsu Photonics) en utilisant une solution diluée d'acide 4-mercaptobenzoïque (MBA) à deux longueurs d'onde d'excitation différentes (633 et 785 nm).

Grâce à des cartographies Raman collectées sur différentes zones de la surface du substrat nous avons déterminé la limite de détection (LOD), la limite de quantification (LOQ) et la sensibilité des différents substrats pour la molécule cible.

Les meilleures performances de détection ont été obtenues avec le substrat Hamamatsu, pour une longueur d'onde d'excitation de 633 nm.

Nous avons utilisé ce substrat pour étudier l'interaction entre un brin d'ADN constitué d'une séquence de 20 Bases identiques (polyT) avec son complémentaire (polyA). En faisant varier la concentration l'orientation des brins d'ADN et leur flexibilité ont été estimées grâce à une analyse statistique des données.

L'augmentation de la concentration en poly A induit une perte de flexibilité du complexe moléculaire polyT/polyA.

Cette étude nous offre une nouvelle approche pour la quantification fiable et l'analyse structurale des molécules biologiques.

Ce travail a été soutenu par le projet Européen DeDNAed (H2020-FETOPEN2018-2020, n° 964248).

References

- [1] N. Guillot, M. Lamy de la Chapelle, Journal of Quantitative Spectroscopy and Radiative Transfer 113, 2321, 2012
- [2] Y. Liu, Y. Zhang, M. Tardivel, M. Lequeux, X. Chen, W. Liu, J. Huang, H. Tian, Q. Liu, G. Huang, R. Gillibert, M. Lamy de la Chapelle, W. Fu, Plasmonics, 15, 743, 2020
- [3] A. Azziz, W. Safar, Y. Xiang, M. Edely, M. Lamy de la Chapelle, Sensing performances of commercial SERS substrates. J. Mol. Struct. 2022, 12, 1248.

Surface-confined host/guest electrochemical switching

Baptiste Chabaud,^a Flavien Sciortino,^a Hugues Bonnet,^a Didier Boturyn,^a
Liliane Guérente,^a and Galina V. Dubacheva^a

^a Université Grenoble Alpes, CNRS, Département de Chimie Moléculaire, UMR-5250,
38041 Grenoble Cedex 9, France. Email: galina.dubacheva@univ-grenoble-alpes.fr

Different systems based on host/guest interactions have been developed for analytical and biomedical applications. One of the strategies uses redox-sensitive interactions between guest ferrocene (Fc) and host β -cyclodextrin (β -CD) [1]. Different molecules and nano-objects have been reversibly assembled on planar surfaces using this approach.

Our objective is to extend this strategy to nanostructures such as nanoparticles (NPs) or patterned nanoarchitectures and to design fluorescence switches based on the tunable NP/fluorophore distance (Fig. 1A). Our recent study on thermosensitive polymers showed the possibility of such switching due to stronger fluorescence quenching at shorter NP/fluorophore distance [2].

In order to apply the β -CD/Fc strategy to nano-objects, it is important to study the efficiency of complexation between Fc and β -CD on the same surface. To this end, we started our study by forming mixed β -CD/Fc monolayers on planar gold surfaces and characterizing their composition and function by surface-sensitive techniques. Thanks to the redox properties of Fc, we characterize its grafting by cyclic voltammetry. Complementary techniques like quartz crystal microbalance (QCM-D) and contact angle goniometry are used to follow β -CD co-immobilization and film rearrangement during applying electrochemical potential. Our first results show successful co-immobilization of Fc and β -CD (Fig. 1B), while their complexation strongly depends on the surface chemistry (diluting thiol, β -CD/Fc ratio, linker nature, etc.). In our next experiments, we will study Fc co-immobilization with fluorescently labeled β -CD on nanostructured surfaces to study the possibility of fluorescence switching upon the formation of the Fc/ β -CD complex.

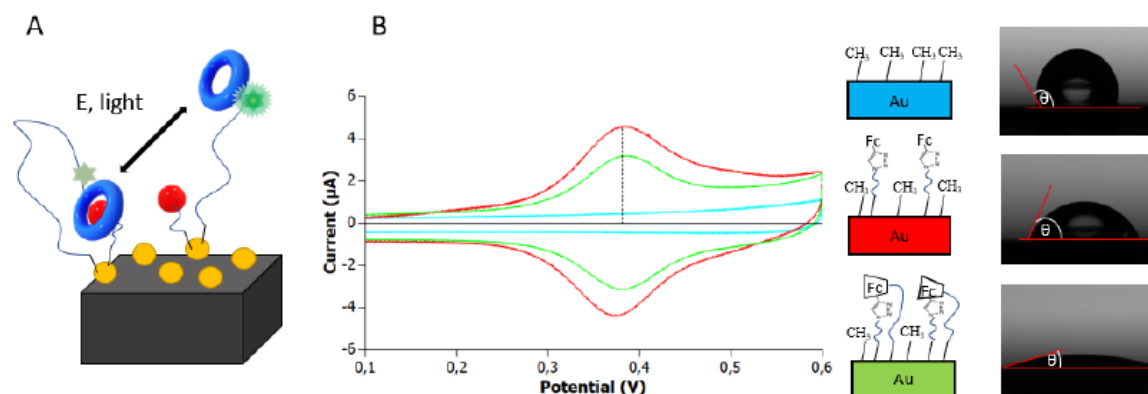


Figure 1: A. Host/guest system on nanostructured surfaces. B. Cyclic voltammetry showing Fc response with and without β -CD (left), supported by contact angle results (right).

- [1] G. Dubacheva et al., *Langmuir*, 26, 13976-13986 (2010)
[2] G. Dubacheva et al., *Langmuir*, 37, 37, 10971-10978 (2021)

Tip-Enhanced Raman Scattering in liquids with side excitation/collection

Patrick Hsia¹ and Marc Chaigneau²

¹*Horiba France SAS, Loos, France*

²*Horiba France SAS, Palaiseau, France*

E-mail: marc.chaigneau@horiba.com

The new breakthrough in Raman nanoscale chemical imaging is measuring in a liquid environment. TERS measurements in liquid will significantly broaden the potential applications of TERS across scientific disciplines such as heterogeneous catalysis, electrochemistry, cellular biology and biomaterials. Implementation of TERS in liquid brings out some instrumental difficulties. AFM-TERS in liquid have been published very recently but mainly in bottom and top optical accesses.

In this contribution, specifics of the TERS setup that enable measurements in liquid with side illumination/collection in order to keep optimal polarization conditions will be discussed: the design of a liquid cell that allows side optical access, the possibility to perform AFM imaging in true non-contact mode in liquid, the alignment procedure of the Raman laser to the AFM-TERS tip in liquid using objective scanner. Thanks to these latest instrumental developments, we will present the nanoscale imaging in liquid of graphene oxide and carbon nanotubes immersed in water. TERS resolution in liquid down to 20 nm is demonstrated along with true non-contact AFM images (fig 1).

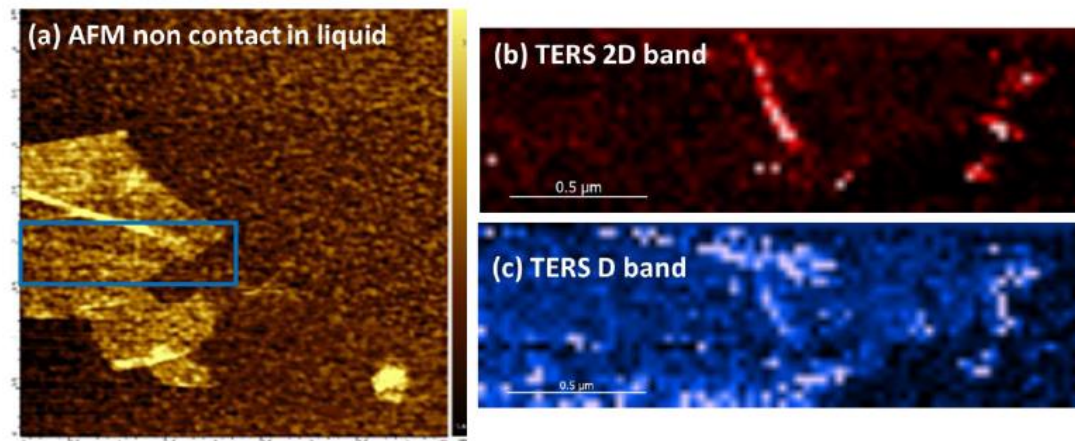


Figure 1: (a) AFM imaging (true non-contact mode) of graphene oxide flake in liquid, (b) TERS map of the 2D band and (c) TERS map of the D band.

This work paves the way to electrochemical reactions that can be followed by tip-enhanced spectroscopies.

Tridimensional micro-nano structuration & functionalisation of substrates for sensitive & fast DEP/SPRI biochip system

O. Andreiev^{1,2,3}, M. Frénéa-Robin², J.-P. Cloarec¹, P. G. Charette³, M. Canva³, J. Marchalot², H. S. Hussain^{1,4}, E. Laurenceau¹

¹ Université de Lyon, Institut des Nanotechnologies de Lyon (INL), UMR CNRS 5270, Ecole Centrale de Lyon, 36 Avenue Guy de Collongue, Ecully cedex 69134, France

² Université de Lyon. Université Claude Bernard Lyon 1, INSA Lyon, Ecole Centrale de Lyon, CNRS, Ampère, UMR5005, 69622 Villeurbanne, France

³ Laboratoire Nanotechnologies Nanosystèmes, Université de Sherbrooke, Sherbrooke, Canada

⁴ Integrated Photonics and Applications Centre (InPAC). Micro Nano Research Facility (MNRF), RMIT University, Melbourne, VIC, 3001, Australia

E-mail: oleh.andreiev@ec-lyon.fr

Surface Plasmon Resonance (SPR) based biosensing systems are well-known conventional biodetection technique of biological and/or biochemical species. However, as many biosensing methods, SPR biosensors sensitivity often is very poor at low analyte concentrations due to slow diffusion-limited target analytes propagation to the sensing surface. The solution for overcoming this limitation could be to increase local target concentration via active mass transport such as electrokinetic effects¹ of dielectrophoresis (DEP) and alternative current electroosmosis (ACEO)^{2,3}. Introducing active mass transport proposes reduction of time of detection, as well as detection threshold of low concentration analytes.

In our project, we suggest utilization of metallic nature of sensing layer (gold) of SPR biosensor as way to induce DEP and ACEO by structuring gold sensing layer and application of non-uniform electric field. Thus, a single chemically functionalized microstructured gold film can be used as both SPR sensing surface and as electrodes to generate DEP and ACEO. Our goal in this work is to investigate the efficiency of developed DEP/ACEO SPRI biosensing, and to look deeply into interaction between components of the biosensor (EK effects, surface functional layer, target object). As of today, we were able successfully test this method for the fast detection of polystyrene beads and Streptavidin molecules, and currently work with further focus on detecting IgG antibody with DEP/ACEO SPRI system.

References:

- (1) Barik, A.; Otto, L. M.; Yoo, D.; Jose, J.; Johnson, T. W.; Oh, S.-H. Dielectrophoresis Enhanced Plasmonic Sensing with Gold Nanohole Arrays. *Nano Letters* 2014, 14 (4), 2006–2012.
- (2) Avenas, Q. Intégration d'une méthode d'actuation électrocinétique sur biocapteur plasmonique. 2018.
- (3) Costella, M.; Avenas, Q.; Frénéa-Robin, M.; Marchalot, J.; Bevilacqua, P.; Charette, P. G.; Canva, M. Dielectrophoretic Cell Trapping for Improved Surface Plasmon Resonance Imaging Sensing. *ELECTROPHORESIS* 2019, 40 (10), 1417–1425.

Wavelength-tunable resonances in plasmonic cavities using a molecular spin-crossover film

Lijun Zhang¹, Karl Ridier¹, Stéphane Calvez², Yuteng Zhang¹, Lionel Salmon¹, Gábor Molnár¹ and Azzedine Bousseksou¹

¹Laboratoire de Chimie de Coordination, CNRS UPR 8241, Toulouse, France

²Laboratoire d'Analyse et d'Architecture des Systèmes, CNRS UPR 8001, Toulouse, France

E-mail: karl.ridier@lcc-toulouse.fr

Molecular spin-crossover (SCO) compounds represent a promising novel class of phase-change materials with high potential for active photonics applications.^[1,2] These transition metal complexes display reversible switching between their low-spin (LS) and high-spin (HS) electronic configurations under various external stimuli (such as temperature, pressure, light radiation, etc.). This switching of the molecular spin state is accompanied by a sizeable change of the optical properties and, in particular, of the refractive index of the material ($\Delta n = 0.2\text{--}0.04$ in the UV-Vis-NIR spectral ranges).^[3]

In this work, we harness this refractive index switching between the LS and HS states in molecular thin films of the SCO complex $[\text{Fe}(\text{HB}(1,2,4\text{-triazol-1-yl})_3)_2]$, which display an abrupt and well-reproducible spin transition around 65°C, to fabricate wavelength-tunable Ag/SCO plasmonic cavities. As shown in Figure 1, the resulting cavities show spectrally tunable resonances due to the spin-crossover phenomenon, providing scope for photonics applications such as switches, sensors, etc.

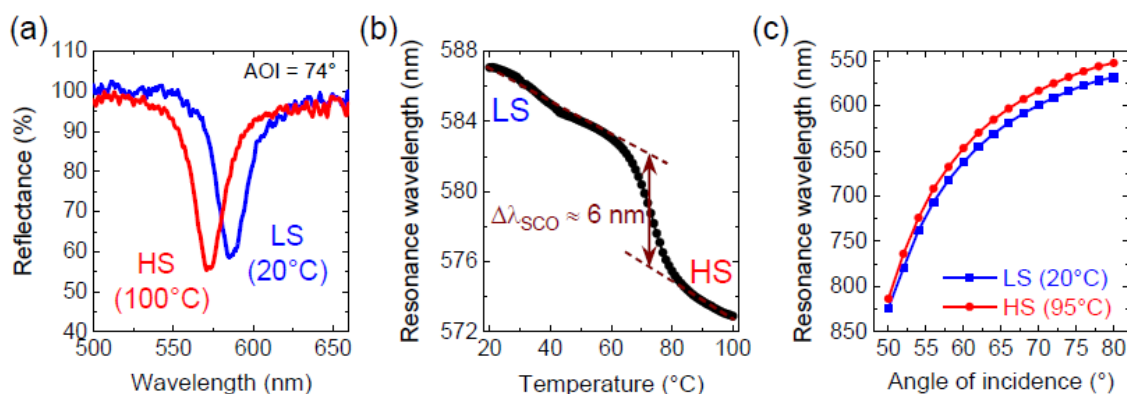


Figure 1. (a) Angle-dependent reflectance spectra of a Ag(73 nm)/SCO(42 nm) plasmonic cavity at 20°C (LS state) and 100°C (HS state). (b) Temperature dependence of the resonance wavelength. (c) Dispersion curves of the cavity in the LS and HS states.

References

- [1] G. Molnár, et al., *Adv. Mater.* **30**, 17003862 (2018)
- [2] G. Félix, et al., *J. Am. Chem. Soc.* **133**, 15342 (2011)
- [3] Y. Zhang, et al., *J. Mater. Chem. C* **8**, 8007 (2020)

Reactive oxygen species generation by laser pulse irradiation of gold nanorods for biomedical applications

S. Mitiche¹, S. Gueffrache¹, S. Marguet², J.-F. Audibert³, R. B. Pansu¹, and B. Palpant¹

¹ Univ. Paris-Saclay, CNRS, ENS-PS, CentraleSupélec, LuMIn, Gif^s/Yvette, France

² Université Paris-Saclay, CEA, CNRS, NIMBE, 91190 Gif-sur-Yvette, France

³ Univ. Paris-Saclay, CNRS, ENS Paris-Saclay, PPSM, 91190 Gif-sur-Yvette, France
E-mail: bruno.palpant@centralesupelec.fr

Gold nanoparticles can produce reactive oxygen species (ROS) under the action of ultrashort pulsed light. While beneficial for photodynamic therapy, this phenomenon is prohibitive for other biomedical applications such as imaging, photo-thermal drug release, or targeted gene delivery. Here, ROS are produced in water by irradiating gold nanorods and silica-coated gold nanorods with near-infrared fs laser pulses and are detected using two fluorescent probes. Singlet Oxygen Sensor Green (SOSG) is the most widely used probe for detecting singlet oxygen ($^1\text{O}_2$). We first show that the emission properties of SOSG and its sensitivity to $^1\text{O}_2$ strongly depend on the concentration of CTAB, a capping agent widely used for nanoparticle synthesis and stabilization [1]. We then demonstrate that a dense silica shell around gold nanorods inhibits the formation of $^1\text{O}_2$ and hydroxyl radical efficiently (Fig. 1). Numerical simulations show that the plasmonic field enhancement at the nanoparticle vicinity is lessened once adding the silica layer. With the multiphotonic ejection of electrons and the Dexter energy transfer between the nanoparticles and $^3\text{O}_2$ being also blocked, all the possible pathways for ROS production are hindered by adding the silica shell around gold nanorods [2], making them safer for a range of biomedical developments.

References

- [1] S. Mitiche, J.-F. Audibert, S. Marguet, B. Palpant, R. B. Pansu, "The effect of gold nanoparticle capping agents on $^1\text{O}_2$ detection by singlet oxygen sensor green", *J. Photochem. Photobio. A: Chem.* **410**, 113170 (2021).
- [2] S. Mitiche, S. Gueffrache, S. Marguet, J.-F. Audibert, R. B. Pansu, B. Palpant, "Coating gold nanorods with silica prevents the generation of reactive oxygen species under laser light irradiation for safe biomedical applications", *J. Mater. Chem. B* **10**, 589 - 597 (2022).

c-AFM and in operando TERS Characterization of Molecular Switching in Organic Memristors

A. Tempez¹, S. Goswami², S. Goswami³, T. Venkatesan², M. Chaigneau¹

¹HORIBA FRANCE SAS, Palaiseau, France

²National University of Singapore, Singapore

³Indian Association for the Cultivation of Science, Kolkata, India

E-mail: marc.chaigneau@horiba.com

Memristive elements are believed to be one of the most promising components for the next generation of electronics for artificial intelligence (AI) and internet of things (IoT). A lot of research effort has also been put in organic memristors because of their nonstochastic and more uniform switching as well as their cheap fabrication cost. However, emergence of organic memristors has been hindered by poor reproducibility, endurance stability scalability and low switching speed. Knowing the primary driving mechanism at the molecular scale will be the key to improve the robustness and reliability of such organic based devices. Deterministic tracking of molecular mechanisms necessitates a nanoscale in-situ spectroscopy in tandem with nanoscopic current measurement that can correlate molecular changes with the current response. This paper reports on the demonstration of a 100% uniform molecular switching mechanism in memristors based on Ru-complexes of azo-aromatic ligands [1-2] using cAFM and TERS measurements: In operando TERS and concurrent conductive AFM allow to characterize the chemical fingerprints of the molecular switching mechanism as voltage across the memristive layer between the AFM tip and a bottom conductive layer is applied while Raman spectra are acquired. A complementary μ Raman study proves a uniform 100% switching of an entire device area.

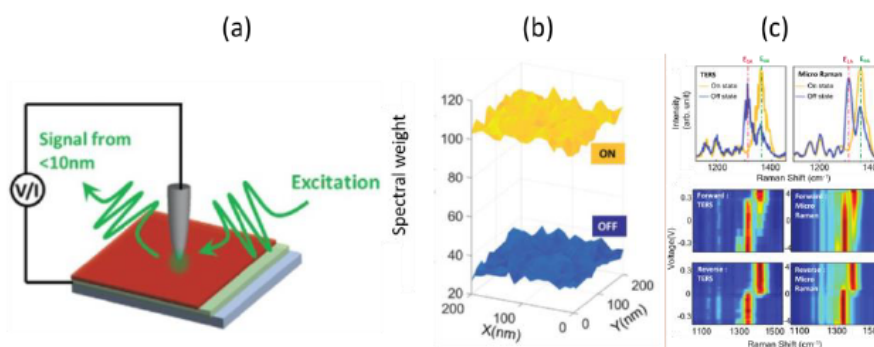


Fig.1: (a) Schematic diagram of concurrent C-AFM and TERS; (b) areal uniformity of spectral response in ON and OFF states, and (c) top: in situ TERS and μ Raman spectra measured in ON and OFF states and bottom: Intensity color plots of spectral voltage dependence in TERS (left) and μ Raman (right) for forward (top) and reverse (bottom) voltage sweeps.

References

- [1] S. Goswami, *et al*, Adv. Mat., 32, 2004370 (2020).
- [2] S. Goswami, *et al*, Nat. Mater., 16, 1216 (2017).

Acoustic vibration modes of gold-silver core-shell nanocuboids

T. O. Otomalo^{1,2}, L. Di Mario³, C. Hamon⁴, D. Constantin⁴, F. Toschi³, K.-V. Do¹, V. Juvé², P. Ruello², P. O’Keeffe³, F. Toschi³, D. Catone³, A. Paladini³, and B. Palpant¹

¹ Univ. Paris-Saclay, CNRS, ENS-PS, CentraleSupélec, LuMIn, Gif^s/Yvette, France

² Inst. des Molécules et Matériaux du Mans, CNRS, Le Mans Univ., Le Mans, France

³ Istituto di Struttura della Materia - CNR, EuroFEL Support Lab. (EFSL), Rome, Italy

⁴ Université Paris-Saclay, CNRS, LPS, Orsay, France

E-mail: bruno.palpant@centralesupelec.fr

Laser-induced heating of plasmonic nanoparticles (NPs), upon their interaction with ultrashort laser pulses, launches acoustic phonon modes due to the lattice expansion via thermo-elastic stress. The vibrations then couple to the localized plasmon modes that can be detected by ultrafast transient absorption experiments. This photo-excited acoustic vibration carries a huge potential for the opto-mechanical applications and for probing mechanical properties of matter at nanoscale. Furthermore, its sensitivity to the amount of matter deposited onto the NPs is a promising prospect for nanoweighting.

We investigate the vibration modes of gold nanorods coated with a silver shell of variable thickness by broadband pump-probe optical spectroscopy. The initial rod-like NPs take on a cuboid shape as the silver thickness increases and results in the appearance of multiple transverse plasmon modes in the near-UV [1]. Analyzing the transient absorption signal by fast Fourier transform reveals vibration modes from 15 to 150 GHz frequency. Simulations allow us to address this vibrational landscape. While bare AuNRs exhibit extensional and breathing modes, the AuNRs@Ag undergo complex motions involving facets, edges, and corners. Their amplitude and frequency depend on the Ag-shell thickness, as the silver load modifies the nanoparticle aspect ratio and mass. Moreover, the acousto-plasmonic coupling results in a wavelength-dependent vibrational spectrum that we elucidate in simulations combining the nanoparticle elastic and optical properties [2].

References

- [1] T. O. Otomalo, L. Di Mario, C. Hamon *et al.*, “Sharp spectral variations of the ultrafast transient light extinction by bimetallic nanoparticles in the near-UV”, *Adv. Opt. Mater.*, **9**, 2001778 (2021).
- [2] T. O. Otomalo, L. Di Mario, C. Hamon, D. Constantin *et al.*, “Acoustic vibration modes of gold-silver core-shell nanoparticles”. *Submitted*.

Nanoplasmonic for probing gas/particle interactions

B. Demirdjian, I. Ozerov, F. Bedu, A. Ranguis, and C. R. Henry

Aix Marseille Université, CNRS, CINaM UMR 7325, Marseille, France

E-mail: benjamin.demirdjian@cnrs.fr

When gas molecules are adsorbed or interact on Au nanodisks (direct sensing) or on nanoparticles (NPs) supported on Au disks (indirect sensing), they modify the local dielectric properties and cause a wavelength shift of the Au disks localized surface plasmon resonance (LSPR).

We measured water adsorption isotherms by following the Au LSPR shift when water molecules adsorb/desorb on Au nanodisks. We were able to detect by direct nanoplasmonic sensing a few hundredths of an adsorbed water monolayer [1].

Then we used indirect nanoplasmonic sensing (INPS) to follow, with a high sensitivity, the interaction of water vapor on soot NPs that are a major contributor to global warming.

Lastly, CO and oxygen adsorption as well as CO oxidation, on Pt NPs, have also been studied by INPS [2]. Due to an optimization of the physical parameters of our plasmonic nanosensor, and coupling with mass spectrometry, we obtain a quantitative and a very sensitive probe that can detect gas adsorption of a few hundredths of a monolayer, even with a very low density of NPs. Moreover, we can use nanoplasmonic sensing at any pressure and temperature.

References

- [1] B. Demirdjian, F. Bedu, A. Ranguis, I. Ozerov, C. R. Henry, *Langmuir* 34, 5381-5385 (2018)
- [2] B. Demirdjian, I. Ozerov, F. Bedu, A. Ranguis and C. R. Henry, *ACS Omega* 6, 13398-13405 (2021)