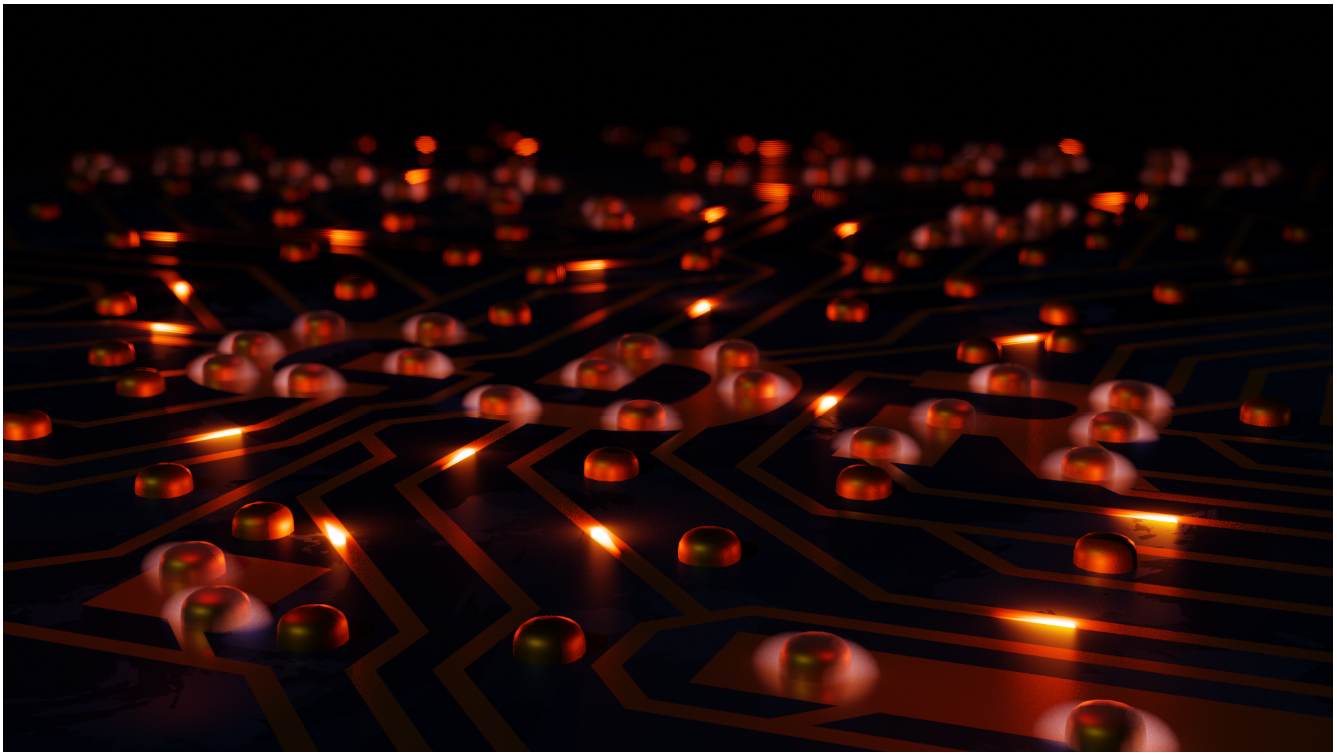
CNRS GDR Groupement de recherche

Plasmonique Active

JOURNÉES PLÉNIÈRES 2021

28 et 29 Juin 2021

Université de Technologie de Troyes



ABSTRACT BOOK

Chères et chers collègues,

Nous sommes ravis de vous accueillir aux journées plénières du GDR Plasmonique Active (CNRS, GDR 2090) à l'Université de Technologie de Troyes (28 et 29 Juin 2021).

Au nom du bureau du GDR, je tiens à remercier en premier lieu Madame Anne-Laure Baudrion, qui a organisé de façon remarquable ces journées, tant sur l'aspect scientifique que logistique. Je tiens également à remercier les nombreux donateurs pour leur soutien financier : la région Grand-Est, la Graduate School NANO-PHOT, la société HORIBA France, le Labex SEAM et bien entendu, l'Université de Technologie de Troyes, qui nous accueille dans ses magnifiques locaux.

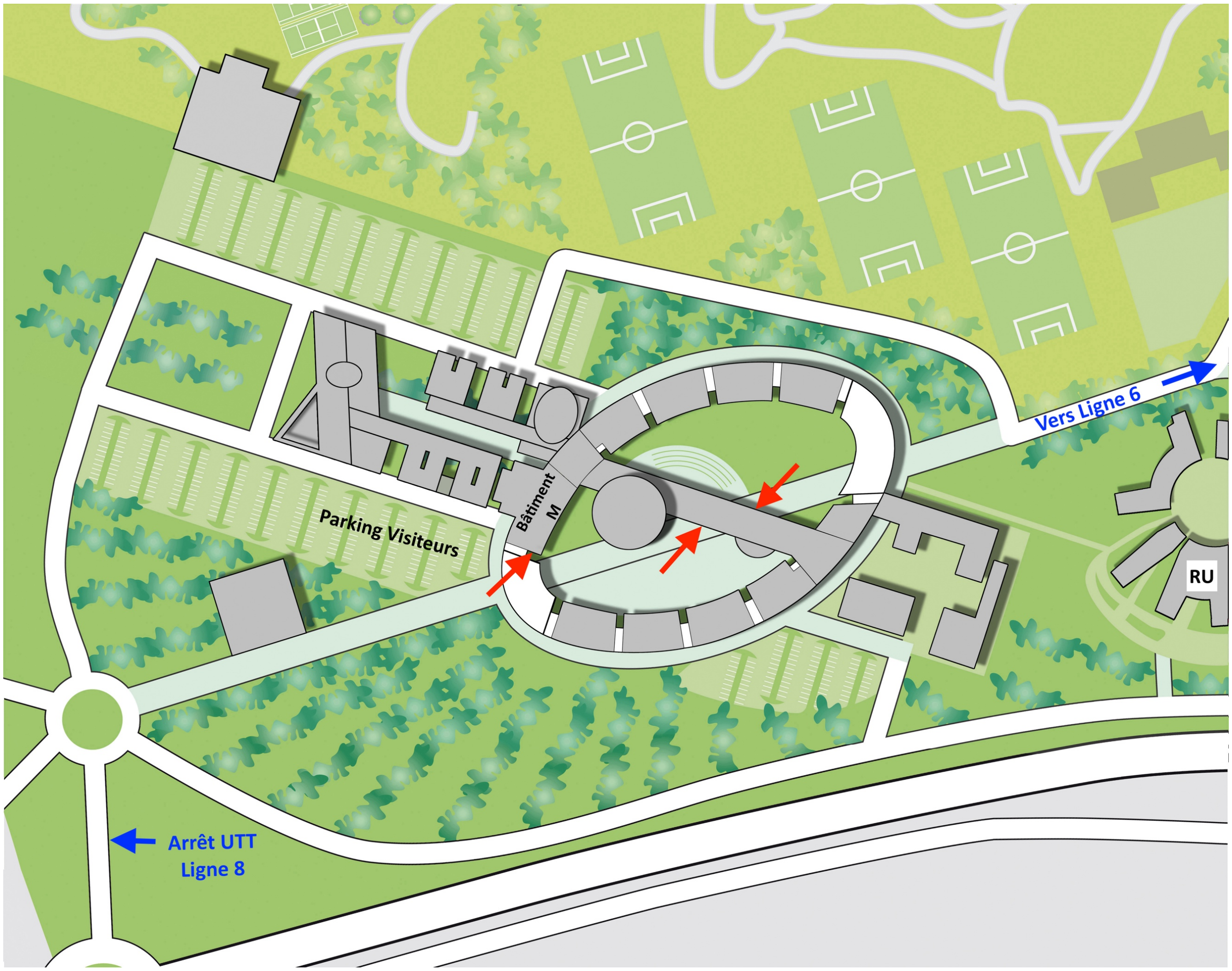
Ces journées seront enfin l'occasion de réunir notre communauté, après une période difficile liée à la crise sanitaire. Au-delà des conférences orales, que ces deux jours nous permettent enfin de retrouver le plaisir de discussions réelles et informelles et de recréer du lien tant sur le plan scientifique qu'amical au sein de notre communauté. Tout cela autour d'une excellente soupe Champenoise !

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

Informations pratiques

Le plan Vigipirate étant actif sur le territoire, l'accès des visiteurs aux bâtiments de l'Université de Technologie de Troyes ne peut se faire que via les portes de l'accueil général et, de manière exceptionnelle pour cet évènement, au bout du bâtiment M, vers le parking visiteurs (cf. flèches rouges ci-dessous).



L'accueil des participants (et la remise des badges) s'effectuera lundi 28 juin de 9h à 11h, puis de 13 à 15h ainsi que le mardi 29 juin de 8h30 à 10h, au comptoir situé au bout du bâtiment M.

La conférence se tiendra en totalité dans le grand amphithéâtre (salle M500) du bâtiment M et la session poster aura lieu dans le couloir face à l'amphithéâtre.

Les pause-café auront lieu en extérieur devant le bâtiment M, tout comme le buffet apéritif qui se tiendra durant la session poster.

Les repas des lundi midi et mardi midi seront pris au Restaurant Universitaire (RU).

cnrs GDR Groupement de recherche
Plasmonique Active

utt UNIVERSITÉ DE TECHNOLOGIE TROYES

Journées plénières 2021

28 et 29 juin 2021
Université de Technologie de Troyes

Programme

Date : Lundi 28 juin 2021

Lieu : Amphi M500 – UTT

9.15 – 10.15	Accueil café - croissants
10.15 – 10.30	Anne-Laure BAUDRION et Nordin FELIDJ – Accueil et introduction
	Axe 1 : Plasmonique accordable – Chair : Anne-Laure Baudrion
10.30 – 11.10	**Jean-Jacques GREFFET – Antenna surface plasmon emission by inelastic tunneling**
11.10 – 11.30	Marion CASTILLA – Colloidal aluminum nanoparticles for UV plasmonic, synthesis and biological applications
11.30 – 11.50	Sébastien FRENKEL – Optical control of plasmonic thermochromic materials
11.50 – 12.10	Fernando GONZALEZ-POSADA – Absorption modulation with semiconductor plasmonic µ-structures from 1.1 to 2.5 THz
12.10 – 12.30	Florian LAMAZE – Dichroïsme circulaire adaptatif pour la détection
12.30 – 14.00	Déjeuner (Restaurant Universitaire)
	Axe 2 : Plasmonique et réactions chimiques – Chair : Leila Boubekeur-Lecaque
14.00 – 14.40	**Claire MANGENEY – New advances in surface functionalization of plasmonic nanoparticles**
14.40 – 15.00	Léa GIMENO - Nano-plasmonic catalyst to enhance catalytic reaction kinetics
15.00 – 15.20	Miguel COMESAÑA-HERMO - Chiral Generation of Hot Carriers for Polarization-Sensitive Plasmonic Photocatalysis
15.20 – 15.50	Pause-café
15.50 – 16.10	Théo GERONIMI JOURDAIN - Experimental evidence of the near-field optical response of hybridized lattice surface plasmon modes
16.10 – 16.30	Shang LI - Attachement of QDs on selected area for hybrid plasmonics
16.30 – 16.50	Marc LAMY DE LA CHAPELLE - Polymérisation radicalaire induite par excitation optique de nanoparticules d'or
16.50 – 17.20	**Table ronde**
17.20 – 19.20	Session Poster et buffet apéritif

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Plasmonique Active

utt Université de Technologie Troyes

Programme

Date : Mardi 29 juin 2021

Lieu : Amphi M500 – UTT

Axe 3 : Plasmonique et transformations physiques – Chair : Marc Lamy De La Chapelle	
09.00 – 09.40	**Alexandre BOUHELIER – Controlling the glowing fate of hot electrons**
09.40 – 10.00	Georges RASEEV – Metal-Insulator-Metal thin film stack: flux enhancement due to coupling of surface plasmon polariton with wave guide modes
10.00 – 10.20	Jérôme PLAIN – Effects of the order-to-disorder transition on plasmonic metasurfaces
10.20 – 10.40	Nathalie DESTOUCHES – Optical properties and applications of laser-induced random plasmonic metasurfaces
10.40 – 11.00	Thomas SIMON – Band-edge emission enhancement in sputtered ZnO thin films with aluminum nanoparticles arrays
11.00 – 11.30	Pause-Café
Axe 4 : Vers des dispositifs plasmoniques intégrés – Chair : Nordin Felidj	
11 :30 – 12.10	**Nadia DJAKER – Gold nanoparticles and biomolecules interactions: Characterization by Scattering Correlation Spectroscopy (SCS)**
12.10 – 12.30	Melissa NAJEM – Wide-Multimodal infrared vibrational spectroscopy from 1.1 to 6.5 µm with Aluminum Bowties
12.30 – 14.00	Déjeuner (Restaurant Universitaire)
14.00 – 14.20	Agnès TEMPEZ – TERS Characterization of Functionalized Gold Nanostructures for Nano-scale Biosensing
14.20 – 14.40	Julien GUISE – Photogenerated metasurface-based THz Modulator
14.40 – 15.00	Florian DELL'OVA – Nonlinear plasmonic cavities for Boolean calculations
15.00 – 15.15	Conclusion et clôture des Journées plénières 2021

Antenna surface plasmon emission by inelastic tunneling

Cheng Zhang[1], Jean-Paul Hugonin[1], Anne-Lise Coutrot[1], Benjamin Vest[1], and Jean-Jacques Greffet[1]

[1] *Université Paris-Saclay, Institut d'Optique Graduate School, CNRS, Laboratoire Charles Fabry, 91127 Palaiseau, France*

The Surface plasmons polaritons are mixed electronic and electromagnetic waves. They have become a workhorse of nanophotonics because plasmonic modes can be confined in space at the nanometer scale and in time at the 10 fs scale. However, in practice, plasmonic modes are often excited using diffraction-limited beams. In order to take full advantage of their potential for sensing and information technology, it is necessary to develop a microscale ultrafast electrical source of surface plasmons. Here, we report the design, fabrication and characterization of nanoantennas to emit surface plasmons by inelastic electron tunneling[1]. The antenna controls the emission spectrum, the emission polarization, and enhances the emission efficiency by more than three orders of magnitude. We introduce a theoretical model of the antenna in good agreement with the results[1,2].

References

[1] Cheng Zhang, Jean-Paul Hugonin, Anne-Lise Coutrot, Christophe Sauvan, François Marquier, Jean-Jacques Greffet, Antenna surface plasmon emission by inelastic tunneling, Nature Communications doi.org/10.1038/s41467-019-12866-3, (2019)

[2] C. Zhang, J.P. Hugonin, J.J. Greffet, C. Sauvan, Surface Plasmon Polaritons Emission with Nanopatch Antennas: Enhancement by Means of Mode Hybridization, ACS Photonics 6, 11, 2788 (2019)

Notes

Colloidal aluminum nanoparticles for UV plasmonic, synthesis and biological applications

Marion Castilla[1], Silvère Schuermans[1], Gil Markovich[2], Uri Hananel[2], Davy Gérard[1], Jérôme Martin[1], Jérôme Plain[1], and Julien Proust[1]

[1]*L2n, UTT & CNRS ERL 7004, 12 rue Marie Curie 10004 Troyes Cedex, France*
[2]*School of Chemistry, Tel-Aviv University, Tel-Aviv, 69978 Israel*

E-mail: `julien.proust@utt.fr`

Aluminum nanostructures appear as a good alternative to gold or silver because of the broad range of their plasmonic resonances (UV to NIR) and their reduced cost[1,2]. The main ways developed to obtain aluminum nanostructures are essentially based on top-down techniques (lithography's, laser ablation…).

Contrary to silver, these structures are very stable in air because of oxygen inclusion, a 3nm native passivation alumina layer is created and act as a protective layer. However, deterioration appears in a solvent for these structures[3].

Nevertheless, a lot of biological experiments occur in the UV range and aluminum nanostructures could help to enhance fluorescence detection. Consequently, it is of first importance to be able to work in organic solvents[4]. The main objective is to synthesis colloidal aluminum nanoparticles with a tunable size and a sufficient stability in solvent in order to use them for biological sensing.

Based on sonochemistry and solvothermal reaction, we created a new way to synthesis aluminum nanoparticles in organic solvent with a short size distribution and a spherical appearance.

By varying controlled parameters, we are able to obtain different size with plasmonic responses in the UV range. The final aim is to do Metal-Enhanced Fluorescence of organic fluorophores for biological applications.

References

[1] Martin, J. Kociak, M. and al. Nano lett. 14,10, pp. 5517-5523 (2004)
[2] Martin, J. Plain, J. Phys. D. Appl.Phys. 48: 184002 (2015)
[3] Zhang, F. Proust, J. and al., J. Phys. Chem. C, 121, 13, pp. 7429-7434 (2017)
[4] Akbay, N. Lakowicz, J.R. and Ray, K. J. Phys. Chem. C, 116, 19, pp. 10766-10773 (2012)

Notes

Optical control of plasmonic thermochromic materials

Sébastien Frenkel[1,2], Khanh-Van Do[2], Boris Le Drogoff[1], Mohamed Chaker[1], and Bruno Palpant[2]

[1] *Institut National de la Recherche Scientifique, Centre Énergie, Matériaux et Télécommunications, 1650 Boul. Lionel-Boulet, Varennes, Québec J3X 1S2, Canada*

[2] *Laboratoire Lumière, Matière et Interfaces, Université Paris-Saclay, CNRS, ENS Paris-Saclay, CentraleSupélec, 91190 Gif-sur-Yvette, France*

E-mail: `sebastien.frenkel@centralesupelec.fr`

Gold or aluminum nanoparticles (NPs) under light irradiation tuned to their localized surface plasmon resonance (LSPR) have the ability to behave as efficient nanoscale heat sources through a series of energy exchange phenomena[1]. Furthermore, thermochromic materials such as vanadium oxide (VO_2) exhibit an insulator-metal phase transition when their temperature increases or when illuminated by ultrashort light pulses[2]. By combining the properties of plasmonic NPs and VO_2 thin films, it is possible to develop hybrid devices with novel photonic or optoelectronic functionalities that can be controlled optically. Our objective is to generate the ultrafast phase transition of VO_2 over a very short range around plasmonic nanoparticles by using ultrashort laser pulses tuned to their LSPR.

In the preliminary study presented here, we have varied the material constituting the NPs (gold or aluminum), the shape (nanodisks or nanorods) and the dimensions of the NPs. Thin films of plasmonic NPs surrounded by VO_2 have been elaborated with millimeter side dimension. Three different configurations are investigated, using different nanofabrication techniques, including electron beam lithography, laser ablation synthesis and plasma etching. The first consists of NPs synthesized on the surface of the VO_2 thin film (1). The second consists of NPs inserted in holes etched in the VO_2 (2). Finally, for the third, we first fabricated the NPs on a quartz substrate and then covered them with a thin layer of VO_2 (3). The first optical measurements show a strong modulation of the LSPR according to these morphological characteristics as well as a stronger photo-induced heating for the configurations (2) and (3), thanks to a stronger interaction between the VO_2 and the NPs. Moreover, by varying the incident wavelength, we demonstrate the link between the LSPR spectrum and the photoconversion efficiency. Finally, the phase transition of VO_2 is observed under ultrashort laser pulse illumination of sufficient intensity.

References

[1] S. Chouteau et al., Appl. Surf. Sci. 554, 149661 (2021).

[2] X. Hou, N. Djellali and B. Palpant, ACS Photon. 5, 3856–3863 (2018).

Notes

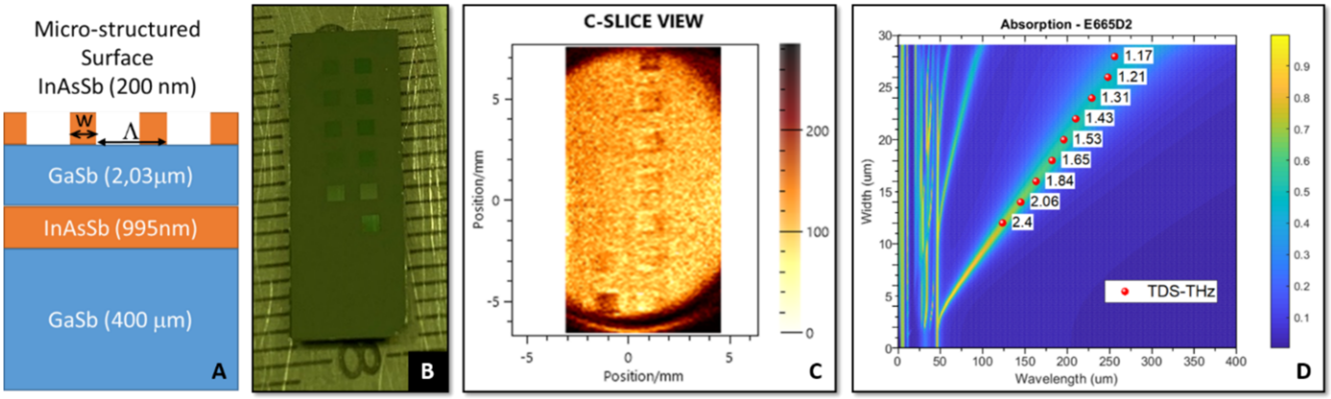
Absorption modulation with semiconductor plasmonic µ-structures from 1.1 to 2.5 THz

F. Gonzalez-Posada[1], D.Coquillat[2], M. Najem[1], P.Loren[1], and T. Taliercio[1]

[1] *IES, Univ Montpellier, CNRS, Montpellier, France*
[2] *L2C, Univ Montpellier, CNRS, Montpellier, France*

E-mail: `fernando.gonzalez-posada-flores@umontpellier.fr`

Terahertz time domain spectroscopy (THz-TDS) remains so far the backbone of terahertz photonics in numerous applications.[1] Plasmonic microstructures and metasurfaces are particularly promising for improving THz spectroscopy techniques and promising for the development of biomedical and environmental sensors.[2] Highly doped semiconductors are suitable for replacing the traditionally-used noble metals, because their plasmonic behaviors are optically tuned with different geometry, size and interactions (gap effect) also in this spectral range. In figure A, a perfect absorber structure based on III-V semiconductor layers is presented on a GaSb commercial substrate template. A photonic absorption peak was targeted in the IR with the thickness of the GaSb spacer on top of a metallic mirror-like doped InAsSb layer. The InAsSb top layer was doped and microstructured to obtain a plasmonic resonance in the THz region. Figure B shows the visible light diffraction of the 1×1 mm^2 micro-structure arrays fabricated by e-beam lithography and dry etching. In figure C, the darkest 1×1 mm^2 squares correspond to an array linewidth of 14 and 16 µm with a constant pitch of 30 µm. Such contrast is related to the coupling between the plasmonic microstructure array and the incident light at a mean frequency region selected in the THz-TDS measurement. Thus, an intense color indicates a higher electric field in the C-slice view scale. In this particular C-slice view, a 2-2.05 THz mean frequency is selected. Finally, in figure D, the THz-TDS measurements of the minimum absorption reached (red dots) correspond with the simulation absorption map calculated by rigorous-coupled wave analysis[3].



Acknowledgement:
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SEA – Region Occitanie (2020-2021)
MUSE – PRIME@MUSE – I-site

References

[1] M. Beard et al. J. of Phys. Chem. B 106, 12345 (2002).
[2] D. M. Mittleman Nature Photonics 7, 666 (2013)
[3] J.-P. Hugonin, & Lalanne. Light-in-complex-nanostructures RETICOLO V8 (2020).

Notes

Dichroïsme circulaire adaptatif pour la détection

F. Lamaze[1], N-B. Bercu[2], J. Béal[1], T. Maurer[1], L. Giraudet[2], and J. Proust[1]

[1] *L2n, Université de Technologie de Troyes & CNRS ERL 7004, Troyes, France*
[2] *LRN, Université de Reims Champagne-Ardenne & EA 4682, 51687, Reims, France*

E-mail: `florian.lamaze@utt.fr`, `julien.proust@utt.fr`

L'utilisation de la déformation d'un substrat flexible comme modulateur du dichroïsme circulaire de nanostructures d'or plasmoniques via le changement de géométrie induit devrait permettre le développement de capteur de déformation à haute sensibilité[1]. La chiralité 2D de nanoparticules d'or sur un substrat entraine un important changement de la résonance plasmon de surface localisée (LSPR) en fonction du sens de rotation d'une source polarisée circulairement. Cela permet l'établissement de la notion de dichroïsme circulaire (DC) qui correspond à la différence de réponse entre polarisation droite et gauche. La chiralité étant fortement dépendante de la géométrie, on peut s'attendre à ce qu'un changement de cette dernière via l'application d'une déformation entraine une importante variation du dichroïsme circulaire. Ici, nous présentons les résultats d'une étude numérique, par la méthode Finite Difference Time Domain (FDTD), d'optimisation du dichroïsme et de sa variation via l'implantation d'un modèle de déformation ainsi que les résultats expérimentaux associés.

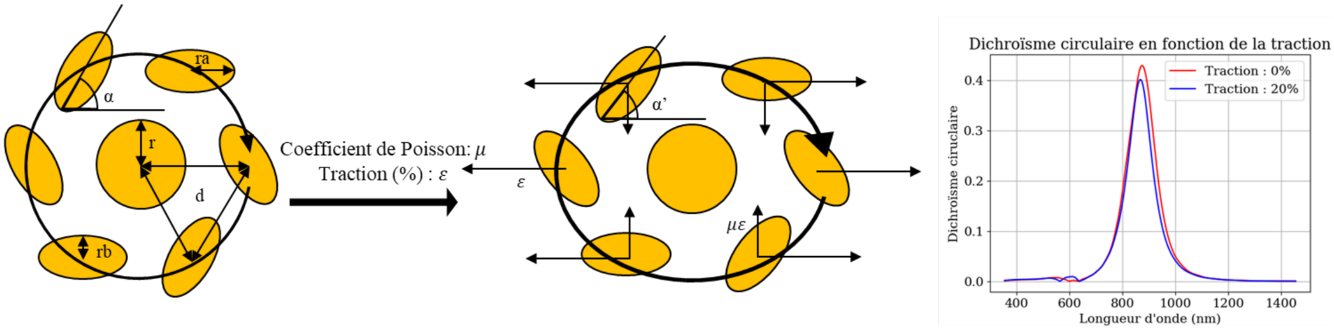

Schéma de la structure[2] associé au modèle de déformation, courbe de la diffusion FDTD et dichroïsme circulaire avant et après 20% de traction

References

[1] U. Cataldi and al. "Growing gold nanoparticules on a flexible substrate to enable simple mechanical control of their plasmonic coupling", Journal of Materials Chemistry C, 2014, 2, 7927

[2] S. Zu, Y. Bao and Z. Fang, "Planar pasmonic chiral nanostructures", Nanoscale, 2016, 8, 3900

Notes

New advances in surface functionalization of plasmonic nanoparticles

T. Geronimi[2], I. Kherbouche[1,2], D. Li[1], P. Nizard[1], D. Onidas[1], Y. Luo[1], A. Lamouri[2], A. Chevillot[2], N. Felidj[2], and C. Mangeney[1]

[1] *LCBPT, UMR 8601, Université de Paris, 75006 Paris, France.*
[2] *ITODYS, UMR 7086, Université de Paris, 75013 Paris, France.*

E-mail: `claire.mangeney@u-paris.fr`

Plasmonics is a growing field of research, at the interface between physics, chemistry, nano-science and biology. Particularly, the use of optically excited plasmonic nanoparticles (NPs) as nanosources of "hot" carriers to activate locally chemical transformations stimulates a high level of interest. In this talk, we will first describe an original strategy for the regioselective functionalization of gold nanoparticles, based on a combination of photo-induced plasmon excitation and aryl diazonium salt chemistry[1,2]. The aryl films derived from diazonium salts are specifically grafted in areas of maximum near field enhancement, as confirmed by numerical calculation based on the discrete dipole approximation method – DDA. This offers exciting perspectives for the nanoscale confinement of functional layers on surfaces for molecular sensing or nanooptics.

We will then explore the potential of aryl diazonium salt-encoded metallic nanoparticles as contrast agents for Surface-Enhanced Raman spectroscopy (SERS) and imaging. Proof-of-concept Raman imaging experiments were performed on cell lines after NP uptake (Fig. 1), highlighting the large potentials of diazonium salt chemistry to design NPs-based SERS labels for multiplex Raman bioimaging[3].

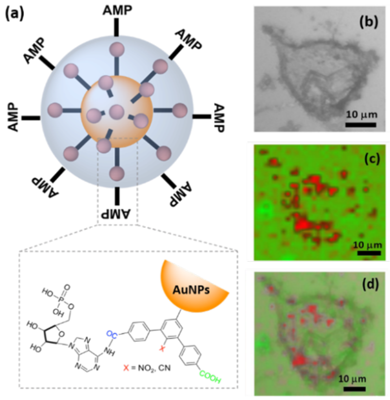

Figure 1. (a) Illustration of gold NPs functionalized by diazonium salts. (b) bright-field optical and (c) Raman image of EGI-1 cell after NPs internalization. (d) Overlaid image of (b) and (c). The distribution of NPs inside cells is marked as red spots, obtained under 633 nm laser excitation.

References

[1] I. Tijunelyte, I. Kherbouche, S. Gam-Derouich, M. Nguyen, N. Lidgi-Guigui, M. Lamy de la Chapelle, A. Lamouri, G. Lévi, J. Aubard, A. Chevillot-Biraud, C. Mangeney, N. Felidj, Nanoscale Horizons, 3, 53 (2018).

[2] M. Nguyen, I. Kherbouche, S. Gam-Derouich, I. Ragheb, S. Lau-Truong, A. Lamouri, G. Levi, J. Aubard, P. Decorse, N. Felidj, C. Mangeney, Chem. Comm., 53, 11364 (2017).

[3] Y. Luo, Y. Xiao, D. Onidas, L. Iannazzo, M. Ethève-Quelquejeu, A. Lamouri, N. Félidj, S. Mahouche-Chergui, T. Brulé, N. Gagey-Eilstein, F. Gazeau, C. Mangeney, Chem. Commun., 56, 6822 (2020).

Notes

Nano-plasmonic catalyst to enhance catalytic reaction kinetics

Léa Gimeno[1], Gennaro Picardi[1], Bernard Humbert[2], Marc Lamy de la Chapelle[3], and Clemence Queffelec[1]

[1] *Université de Nantes, CNRS, CEISAM, UMR 6230, F-44000 Nantes, France 2 IMN, Institut des Matériaux Jean Rouxel, Université de Nantes, 2 Rue de la Houssiniére, 44322 Nantes, France*

[2] *Laboratoire IMMM, UMR CNRS 6283, Université du Mans, Avenue Olivier Messian, 72085 Le Mans France*

E-mail: `lea.gimeno@univ-nantes.fr`

Plasmonic is a very active research field in several domains especially enhanced spectroscopy, biological and chemical imaging and lithographic fabrication. Plasmonic enhancement of synthetic reactions using irradiation of noble metal nanoparticles (NPs) has been rather limited to stoichiometric organic transformations and has been more recently used to enhance catalytic reaction rate. The use of light such as LED, a low-cost energy, to irradiate noble metal NPs in catalysis allows milder condition reactions and leads to shorter reaction time with better selectivity. In our research project, we aim to develop new nano-catalysts to enhance the kinetic of the Henry reaction using localized surface plasmon resonance (LSPR).[1] This nano-catalyst will consist of colloidal gold NPs with an organometallic complex grafted onto the surface. This new nano-catalyst will allow us to combine two major effectsin the catalytic reaction. On one hand, a localized surface plasmon effect (LSP)[2] induced by illuminating gold nanoparticles with green LED. On the other hand, the organometallic catalyst effect generated by a bipyridine based copper(II) complex bearing a dithiolane anchoring group grafted on gold nanoparticles surfaces to assure a strong covalent bonding. Henry reaction is a C-C bound formation reaction between nitroalkanes and aldehydes or ketones with usually slow kinetics, classically conducted in presence of a base or copper(II) complexes.[3] Our preliminary results on Henry reaction seem to suggest a substantial increase in thekinetic's reaction in the presence of the irradiated nano-catalyst, results supported by real time Surface-Enhanced Raman Spectroscopy (SERS) and NMR tracking experiments.

References

[1] A.Mooreet al, Chem. Rev.,986–1041(2020)
[2] Gregory V. Hartland, Chem. Rev., 3858–3887 (2011)
[3] Q. Song et al, C. R. Chimie, 215–222(2015)

Notes

Chiral Generation of Hot Carriers for Polarization-Sensitive Plasmonic Photocatalysis

Yoel Negrín-Montecelo’, Artur Movsesyan[2], Jie Gao[3], Sylvain Nlate[3], Emilie Pouget[3], Reiko Oda[3], Alexander O. Govorov[2], Miguel A. Correa-Duarte[1], and Miguel Comesaña-Hermo[4]

[1] *Department of Physical Chemistry, Biomedical Research Center (CINBIO), Universidade de Vigo, 36310 Vigo, Spain*
[2] *Department of Physics and Astronomy, Nanoscale and Quantum Phenomena Institute, Ohio University, Athens, Ohio 45701, United States*
[3] *Chimie et Biologie des Membranes et des Nanoobjets (CBMN), CNRS, Université de Bordeaux, Bordeaux INP, UMR 5248, 33607, Pessac, France*
[4] *Université de Paris, ITODYS, CNRS, UMR 7086, 15 rue J-A de Baïf, F-75013 Paris, France*

E-mail: `miguel.comesana-hermo@u-paris.fr`

It has been recently predicted that the formation of plasmonic assemblies with chiroptical activities can induce an asymmetric response on the hot charges generated via electromagnetic excitation.[1,2] In this manner, hot electrons and holes could be used for the development of polarization-sensitive photochemistry. In the present work we use silica nanoribbons as chiral templates for the controlled assembly of plasmon-based photocatalysts,[3,4] leading to the formation of hybrid materials with asymmetric catalytic features. More precisely, we demonstrate that an improved reaction yield can be obtained when the helicity of the circularly polarized light used for the activation of the plasmonic component matches the handedness of the chiral substrate. Both experiments and theory demonstrate that the chiroptical activity of the plasmonic assembly induces an asymmetric density of hot charges that depends on complex inter-particle interactions. Such results can open the door to new applications in the fields of chirality and photocatalysis, particularly towards plasmon-induced chiral photochemistry.

References

[1] Khorashad, JACS 142, 4193 (2020)
[2] Liu, Nano Letters 19, 1395 (2019)
[3] Okazaki, ACS Nano 8, 6863 (2014)
[4] Cheng, ACS Nano 11, 3806 (2017)

Notes

Experimental evidence of the near-field optical response of hybridized lattice surface plasmon modes

T. Geronimi Jourdain[1], M. Braïk[2], A. Belkhir[2], S. Lau Truong[1], S. Gam-Derouich[1], A. Chevillot-Biraud[1], L. Boubekeur-Lecaque[1], C. Mangeney[3], J. Aubard[1], G.Lévi[1], and N. Félidj[1]

[1] *Université de Paris, Laboratoire ITODYS, CNRS, F-75006 Paris, France*
[2] *Université Mouloud Mammeri de Tizi-Ouzou, LPCQ, BP 17 RP, 15000 Tizi-Ouzou, Algeria,*
[3] *Université de Paris, LCBPT, CNRS, F-75006 Paris, France*

E-mail: `nordin.felidj@univ-paris-diderot.fr`

The tuning of hybridized localized surface plasmon (LSP) modes in coupled metallic nanostructures has appeared recently as an emerging strategy to control their optical properties. When the nanostructures are assembled in periodic arrangements, they support collective plasmon lattice resonances resulting from long-range interaction, which are radically different from LSP resonances observed for coupled nanostructuresin a short-range interaction. Similarly to the hybridization of LSP resonances, a hybridization of surface lattice (SL) plasmon resonances can be observed[1]. In this talk, we will describe plasmonic platforms made of binary arrays with unit cells composed of two gold disks of distinct diameters. The hybridization of SL resonances can be described as the electromagnetic analog of the molecular orbital theory, with the emergence of bonding and anti-bonding modes, similarly to the hybridized LSP modes observed in short-range interactions. We experimentally evidenced the near-field optical response of the bonding and anti-bonding modes of the hybridized lattice surface plasmon, through a strategy based on plasmon-induced surface functionalization derived from diazonium salts[2]. This strategy allowed us to map the intensity of the local electric field. These results, supported by FDTD calculations, open promising prospects for nanooptics.

References

[1] M. Braïk, T. Geronimi Jourdain, I. Ragheb, A. Belkhir, S. Lau Truong, S. Gam-Derouich, A. Chevillot-Biraud, L. Boubekeur-Lecaque, C. Mangeney, J. Aubard, G. Lévi and N. Félidj (submitted, 2021)

[2] I. Kherbouche, D. MacRae, T. Geronimi Jourdain, F. Lagugné-Labarthet, A. Lamouri, A. Chevillot Biraud, C.Mangeneyand, N.Félidj, Nanoscale (accepted, June 2021)

Notes

Attachement of QDs on selected area for hybrid plasmonics

S. Li[1], S. Garzandat[1], T. Geronimi[2], D. Ge[1], A. Verneuil[1], H. Chen[1], M. Chen[1], A. Issa[1], A. Baudrion-Beal[1], P.-M. Adam[1], N. Felidj[2], Y. Luo[3], C. Mengeney[3], and R. Bachelot[1]

[1] *University of Technology of Troyes, L2n ERL CNRS 7004, Troyes, France*
[2] *Paris University, ITODYS, UMR CNRS 7086,Paris, France*
[3] *Paris University, LCBPT, UMR CNRS 8601Paris, France*

E-mail: `renaud.bachelot@utt.fr`

To meet the fast development of optical and quantum computing, high quality advanced integrated nano-sources of light are desired as one of the basic elements. In particular, hybrid nano-sources, coupling together QDs and metal nanoparticles, is expected to achieve small size, stable performanceand high efficiency at the same time.[1] However, the control of the nanoscale spatial distribution of QDs on the metal surface is still problematic, albeit crucial for efficient integrated hybrid nano-sources. Surface chemistry of diazonium salt has proved to be a good method to functionalize selected areason metal nanoparticle.[2] Functionalized QDs could be selectively attached on thes pre-selected functionalized areas, resulting in a controlled anisotropy in the gain medium of the hybrid plasmonic nanosource.

In this paper, we study the possibility to attach deposited QDs onselected areas whose surface is functionalized by two different kinds of diazonium salt: DNO_2 and DCOOH. Functionalized QDs have positive surface charge in aqueous solution, which is supposed to attach to DCOOH by charge adsorption, while no interaction is expected with DNO_2 functionalized area. Table 1 shows an example of results, when QD deposition time increased from 5 min. to 60 min. More QDs attached to DCOOH area. For DNO_2 area, the number of attached QDs (probably through Van der Wall forces) is less sensitive to the deposition time. Our results show the possibility of selected attachment of QDs by surface chemistry for future plasmonic nanosources.

Deposition time	Number of photons per surface area for DCOOH (photons/µm^2)	Number of photons per surface area for DNO_2 (photons/µm^2)
60 mins	325,736.8 ± 50,136.6	138,669.9 ± 19,870.9
30 mins	287,220.9 ± 106,321.2	157,646.9 ± 27,974.1
15 mins	259,901.5 ± 24,898.7	237,339.9 ± 32,129.6
5 mins	113,236.6 ± 6,133.2	131,848.7 ± 19,182.1

Photoluminescence measurement under blue excitation. Number of photons per surface area for DCOOH and DNO_2 with different QDs deposition.

References

[1] X. Zhou, et al., Nanoletters, 15, 7458 (2015)
[2] I. Tijunelyte, et al., Nanoscale Horiz., 3, 53 (2018)

Notes

Polymérisation radicalaire induite par excitation optique de nanoparticules d'or

A. Ali[1], F. Amiard[1], S. Piogé[1], and M. Lamy de la Chapelle[1]

[1] *Institut des Molécules et Matériaux du Mans-IMMM (UMR CNRS 6283), Le Mans Université, Le Mans, France*

E-mail: `marc.lamydelachapelle@univ-lemans.fr`

Grace à leurs propriétés optiques et plasmoniques remarquables, les nanoparticules métalliques (NPs) peuvent provoquer différents phénomènes physiques comme une élévation de température, la création d'une nano-source exaltée de lumière ou le transfert d'électrons chauds vers des molécules.[1] De tels phénomènes peuvent être valorisés pour modifier des molécules, activer des réactions chimiques ou bien améliorer leurs cinétiques ou leurs rendements.[2]

Notre travail propose d'explorer un nouveau processus d'activation radicalaire (formation de radicaux primaires) de polymérisation via l'exploitation des propriétés plasmoniques des NPs d'or afin d'élaborer des polymères biens définis. Le plasmon est donc utilisé pour induire la formation de radicaux primaires nécessaires à la polymérisation de monomères vinyliques sous irradiation lumineuse (λ = 458, 515, 611 ou 630 nm). Une étude systématique des conditions expérimentales (concentration en NPs, taille des NPs, position de la résonance plasmon, concentration en monomère *N,N*-diméthylacrylamide) d'un tel système nous a permis de démontrer que le plasmon améliore les performances de synthèse (cinétique et rendement de polymérisation) à 458 nm et que ces performances sont optimales à 515 nm, longueur d'onde proche de la résonance plasmon des NPs d'or. Au contraire, aucun effet du plasmon sur la réaction de polymérisation n'a été détecté à 611 et 630 nm (longueurs d'ondes hors résonance). De plus, même si la concentration en NPs influence la cinétique de polymérisation, il est à noter qu'une très faible concentration en NPs de quelques pmol/L est suffisante pour identifier des performances cinétiques intéressantes.

Cette étude permet de mieux comprendre les phénomènes mis en jeu lors de l'activation radicalaire en polymérisation photo-induite et d'évaluer l'influence réelle du plasmon. Grace à cette étude, les paramètres plasmoniques tel que la position de la résonance sont identifiés comme ceux impliqués dans le processus de l'activation radicalaire en polymérisation.

References

[1] Baffou, G. et al., Chemical Society Reviews 43, 3898 (2014)

[2] Xiao, M. et al., Journal of Materials Chemistry A 1, 5790 (2013)

Notes

Controlling the glowing fate of hot electrons

A. Agreda[1], D. K. Sharma[1], F. Dell'Ova[1], K. Malchow[1], G. Colas des Francs[1], E. Dujardin[2], and A. Bouhelier[1]

[1] *Laboratoire Interdisciplinaire Carnot de Bourgogne, Université de Bourgogne Franche-Comté, Dijon, France*

[2] *CEMES CNRS UPR 8011 and Université de Toulouse, 29 rue J. Marvig, 31055 Toulouse, France*

E-mail: `alexandre.bouhelier@u-bourgogne.fr`

Light illumination of a metal generates energetic electron-hole pairs upon photon absorption by the carriers. These energetic out-of-equilibrium carriers are referred as hot carriers. An emerging interesting facet is to utilize these hot carriers for producing minute sources of light by taking advantage of the hot carriers' relaxation process within the metal[1]. A few hundred of femtoseconds after the absorption event the temperature of electron gas reaches thousands of kelvin[2] leading to an emission of a thermal electromagnetic continuum characterized by an ultrafast kinetics (ps) largely surpassing the dynamics of standard thermal sources (µs)[3]. We show in this work the plasmonic local density of states, given by the material properties and the structural shape, defines the hot-electron generation efficiency as well as the spatial distribution of the light continuum in the system[4,5]. Using this strategy, we design specific plasmonic elements sustaining a rich plasmon modal landscape enabling the realisation of universal and reconfigurable logic gates[6]. We then introduce another degree of control and demonstrate the successful command of the light continuum by electrical means. Specifically, the emission depends on the hot-electron temperature which is directly influenced by electrically induced charge density variations[7]. Engineering of the optical and static electric fields generated in the nanostructures leads to full control in space and time of the electronic temperature, influencing thereby the spectral and spatial characteristics as well as the photon generation yield.

Acknowledgements

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References

[1] Saavedra, J. R. M., et al. ACS Phot. 3, 1637-1646 (2016).

[2] Hou, X., et al., ACS Phot. 5, 3856-3863 (2018).

[3] R. Méjard, et al. ACS Phot. 3, 1482-1488 (2016).

[4] S. Viarbitskaya, et al., A. Phys. Rev. Lett. 115, 197401 (2015)

[5] A. Cuche, et al. Opt. Comm. 387, 48-54 (2017)

[6] U. Kumar et al. ACS Phot 5, 2328–2335, (2018).

[7] A. Agreda et al., ACS Phot, 7, 2153-2162 (2020).

Notes

Metal-Insulator-Metal thin film stack: flux enhancement due to coupling of surface plasmon polariton with wave guide modes

Georges Raseev[1] and Moustafa Achlan[1]

[1] *Université Paris-Saclay, Univ. Paris-Sud, CNRS, Institut des Sciences Moléculaires d'Orsay, Orsay, France*

E-mail: `georges.raseev@universite-paris-saclay.fr`

A theoretical study is presented of the dispersion of surface plasmon polariton (SPP) and wave guide (WG) modes of a metal-insulator-metal (MIM) thin film stack. This is the continuation of a combined experimental and theoretical work performed in a preceding study[1]. In this work[2] we study the dispersion of the reflectance and of the transmitted flux, originating from a local excitation source, of an asymmetric MIM air-Au-SiO_2-Au-Ti-glass and glass-Au-SiO_2-Au-Ti-air material systems in the infrared and visible spectral region for a wide range of SiO_2 and gold thicknesses, d_{SiO_2} and d_{Au}. In comparison to reference stacks of air-Au-glass, air-SiO_2-glass, glass-Au-air and glass-SiO_2-air, between 1.4 and 2.0 eV, the transmitted flux intensity is enhanced 12 or 25 times, in the emission direction of the in-plane wave vector $k_\rho/k_0 \sim 1.05$ and for a thickness of d_{SiO_2} between 300 and 700 nm and d_{Au} between 15 and 40 nm respectively. This enhancement is attributed to the coupling, through the avoided crossings, of the SPP_{air} and WG modes. As the fields of the SPP_{air} and WG modes are located in different regions of space the enhancement is nearly independent of the number of nodes in the WG mode. In summary we have identified sets of parameters giving rise to the observables enhancement. Therefore the present MIM thin film stack is a simple and a versatile system for the use in applications where an enhancement in required.

References

[1] S. Cao, M. Achlan, J-F. Bryche, P. Gogol, G. Dujardin, G. Raseev, E. Le Moal and E. Boer-Duchemin, Opt. Express 27, 33011 (2019)

[2] G. Raseev and M. Achlan, Journal of Physics D: Applied Physics, 53, 505303 (2020)

Notes

Effects of the order-to-disorder transition on plasmonic metasurfaces

Feifei Zhang[1], Feng Tang[1], Xiaolun Xu[1], Pierre-Michel Adam[1], Jérôme Martin[1], and Jérôme Plain[1]

[1] *L2n, CNRS ERL 7004 and Université de technologie de Troyes, France*

E-mail: `jerome.plain@utt.fr`

We have studied the effect of a uniform disorder on plasmon resonances numerically and experimentally on arrays of aluminum (Al) nanoparticles. Thus, we have studied three types of disorder in Al plasmonic metasurfaces: a displacement disorder, a size disorder and finally a rotation disorder.

The random variation in the location or size of each Al nanodisk in the plasmonic metasurface induces a broadening and a reduction of their plasmon resonances without significantly changing its energy. Furthermore, by rotating each Al nanorod in the plasmonic crystal at a random angle, the polarization dependence of the plasmonic resonances gradually decreases with the rotational disorder. Through these three types of Al metasurfaces, an in-depth understanding of the influence of small manufacturing deviations on the optical properties of metasurfaces is supported[1].

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References

[1] Feifei Zhang, Feng Tang, Xiaolun Xu, Pierre-Michel Adam, Jérôme Martin and Jérôme Plain, Influence of order-to-disorder transitions on the optical properties of the aluminum plasmonic, Nanoscale 12, 23173 (2020)

Notes

Optical properties and applications of laser-induced random plasmonic metasurfaces

N. Sharma[1], N. Dalloz[1,2], D. Le[1], B. Eles[1], M. Hébert[1], and N. Destouches[1]

[1] *Laboratoire Hubert Curien, CNRS UMR 5516, Institut d'Optique Graduate School, Univ Lyon, 42000 St-Etienne, France*

[2] *HID Global CID SAS, 48 rue Carnot, 92150 Suresnes, France*

E-mail: `nathalie.destouches@univ-st-etienne.fr`

Plasmonic color generation has attracted intensive attention because of the high color contrast and long lifetime of metal nanostructures protected by dielectric cover. Strong technological impact has been predicted, however industrial applications are still limited. Recently, the singular dichroic properties of plasmonic colors have been soundly used to develop image multiplexing. Several images can then be encoded in a single plasmonic metasurface in such a way that they could be revealed independently by altering the conditions of observation of the metasurface.

The technologies developed for image multiplexing so far, mainly create holographic images by controlling the polarization, amplitude and phase of reflected and transmitted light through interaction with well-controlled plasmonic metasurfaces produced by electron beam lithography. Printed image multiplexing was also implemented to observe the different images on the metasurfaces themselves, with an optical microscope under white light by changing the polarization of light.

To print plasmonic colors on large areas, laser processing can be considered as a cost-effective, rapid and flexible technology. But, it usually creates random plasmonic metasurfaces characterized by statistical parameters (like size distribution, average period, etc.) that are often difficult to measure and, which require prohibitive calculation to simulate their electromagnetic response. Furthermore, the prediction of these statistical parameters from the knowledge of laser processing parameters is not possible by physical models yet. This could appear as incompatible with implementing image multiplexing, which requires a high control of color prediction in various modes of observation.

Here, we demonstrate that printed image multiplexing can be implemented by laser processing with random plasmonic metasurfaces and produce images that can be demultiplexed by naked eye under natural light by simply rotating the surface[1].

References

[1] N. Destouches, N. Sharma, M. Vangheluwe, N. Dalloz, F. Vocanson, M. Bugnet, M. Hébert, J. Siegel, "Laser-empowered metasurfaces for white light image multiplexing", Adv. Func. Mater., 2010430 (2021)

Notes

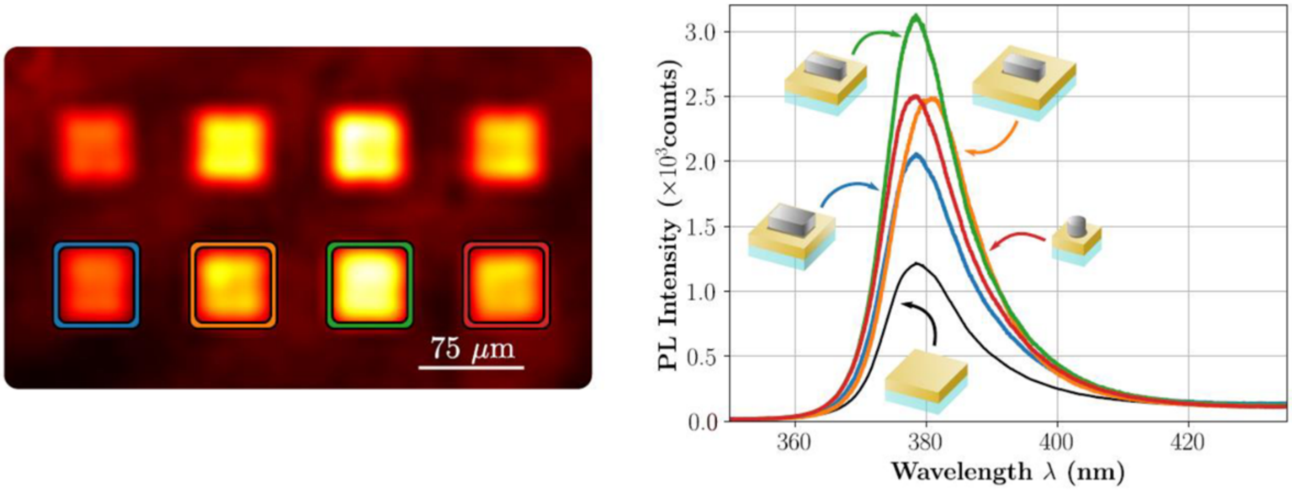
Band-edge emission enhancement in sputtered ZnO thin films with aluminum nanoparticles arrays

T. Simon[1], J. Béal[1], S. Kochtcheev[1], A. Rumyantseva[1], D. Gérard[1], and J. Martin[1]

[1] *L2n, Université de Technologie de Troyes & CNRS ERL 7004, Troyes, France*

E-mail: `thomas.simon@utt.fr`, `jerome.martin@utt.fr`

Les nanostructures d'aluminium sont désormais considérées comme l'un des éléments les plus efficaces pour obtenir des résonances plasmoniques dans le bleu-UV[1]. De plus, il est possible d'obtenir des modes hybrides entre des résonances plasmon de surface localisée (LSPR) et des anomalies de Rayleigh, avec des réseaux de nanoparticules métalliques. Ces modes de réseaux possèdent une forme type Fano plus fine que la résonance LSP d'une particule isolée[2]. Ici, nous présentons des structures de nanoparticules d'aluminium fabriquées par lithographie électronique, sur une fine couche d'oxyde de Zinc déposée par pulvérisation assistée par plasma, dans le but d'exalter la photoluminescence du semi-conducteur par le biais de modes de réseaux.



Mesures de photoluminescence UV — cartographie de photoluminescence de l'échantillon à 378 nm et spectres de photoluminescence correspondants

References

[1] D. Gérard and S. Gray, "Aluminium plasmonics," Journal of Physics D: Applied Physics, 2015.

[2] D. Khlopin, F. Lauxet al., "Lattice modes and plasmonic linewidth engineering in gold and aluminum nanoparticle arrays," JOSA B, 2017.

Notes

Gold nanoparticles and biomolecules interactions: Characterization by Scattering Correlation Spectroscopy (SCS)

R. Dekhili[1], M. Chalal[1], Q. Liu[1], N. Harou[1], H. Liu[2], X. Li[2], M. Lamy de la Chapelle[3], J. Spadavecchia[3], and N. Djaker[1]

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

[2] *Department of Hepato-Biliary Surgery, Shenzhen University General Hospital, Shenzhen, China*

[3] *Institut 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`

The Gold nanoparticles (GNP) possess exceptional physico-chemical properties, which allow their use in many biomedical fields, such as drug delivery and photothermal therapy[1,2]. Generally, two major morphologies are used for the biomedical applications: isotropic-shapes as gold nanospheres (SGN) and anisotropic-shapes or branched-shapes (BGN). The main advantage of BGN is the presence of different surface energies due to different edges leading to a strong enhancement of the electromagnetic field[3-5]. Moreover, BGN compared to SGN offer a greater surface to volume area for functionalization especially in the case of nanovectors and biosensors applications[6]. Recently, sensitive techniques based on the measurement of the hydrodynamic radius of the GNP before and after interaction with biomolecules in a very small detection volume (∼1femtoLiter) were developed. While the fluorescence correlation spectroscopy needs fluorescent labelling, scattering correlation spectroscopy (SCS) is the most suitable for GNP characterization because of their strong optical scattering properties[3-5]. This technique allows studying the interaction of several biomolecules (aptamers, proteins) with GNP at a very high sensitivity. In the case of protein-GNP interaction, the SCS is a powerful tool to explore several parameters such as protein orientation, binding affinity (K_D) and cooperativity (n) regarding the GNP surface[7]. Moreover, biosensors based on SCS detection will be shown for the Cu-Zn SuperOxide Dismutase (SOD1) detection. SOD1 is a major antioxidant enzyme, which the activity and expression change significantly in gastric cancer patients[6]. GNP synthesized and functionalized with aptamers for a high selectivity of the SOD1 will be shown. SCS technique allows the detection of several biomolecules and determines the relevance of such nanobiosensor for the disease diagnosis.

References

[1] H. Liu, et al., Part. Part. Syst. Charact., 1700299 (2018).
[2] H. Moustaoui, et al., ACS Appl. Mater. Interfaces, 8(31): p.19946 (2016).
[3] N. Djaker, et al., J. Phys. Chem. C, 120(21): p. 11700 (2016).
[4] D. Issaad, et al., J. Phys. Chem. C, 121(33): p. 18254 (2017).
[5] H. Moustaoui, et al., 123(28): p. 17548 (2019).
[6] R. Rekhili, et al., Acs Omega, 5(23): p. 13851 (2020).
[7] H. Moustaoui, et al., Nanoscale, 11(8): p. 3665 (2019).

Notes

Wide-Multimodal infrared vibrational spectroscopy from 1.1 to 6.5 µm with Aluminum Bowties

M. Najem[1], F. Carcenac[2], F. Gonzalez-Posada[1], and T. Taliercio[1]

[1]*IES, Univ Montpellier, CNRS, Montpellier, France*
[2]*LAAS, CNRS, Toulouse, France*

E-mail: `melissa.najem@umontpellier.fr`

Vibrational surface-enhanced spectroscopy is a promising application in the plasmonics field, where metallic nanoantennas (NA) are tailored to provide local electromagnetic field localization and enhancement for biomedical applications.[1] To cover a wide IR active range, from 1.1 to 6.5 µm, Al NA were picked as low-cost material with promising optical quality, CMOS compatible, and excellent properties for sensing. Figure A shows a metal-insulator-metal (MIM) with respective thicknesses of 100 nm of Al, 20 nm of SiO_2, and 50 nm Al NAs.

Figure B shows the single unit cell of the NAs array formed of Al Bowties (BTs). To investigate the spectral response of these periodic Al-BTs, a numerical FDTD solver (Lumerical) was employed, where Maxwell's equations were discretized in both time and space. The Al-BT array was always polarized along y-axis to enhance the electrical field, as the gap strongly localizes the field.[2] For a wide-coverage purpose and to tune their localized surface plasmon resonance (LSPR) at different spectral positions, the side length (L) of each Al-triangle was swept from 0.3 to 2 µm with a step of 0.1 µm (Fig.C). The distance, d, between these triangles was maintained at 100 nm. For each L value, one main plasmonic resonance peak was detected which is usually referred to as a strong dipolar coupling. This first-order plasmonic resonance is always situated at the highest wavelength, then higher orders of resonance and other diffraction peaks appear representing the periodicity triggered along y-axis.

Al-BTs array were fabricated by electron-beam lithography followed by metallization and lift-off process; then were characterized under 36× IR Fourier Transform IR (FTIR) spectrometer. Figure D shows a good agreement between simulation (FDTD) and experimental (FTIR). The detected LSPR peaks appear at the exact simulated spectral position. Such a result is extremely encouraging for a lab-on-chip detection vision of functional groups and fingerprints of any bio-molecule in this propitious IR range using a single plasmonic platform.[3]

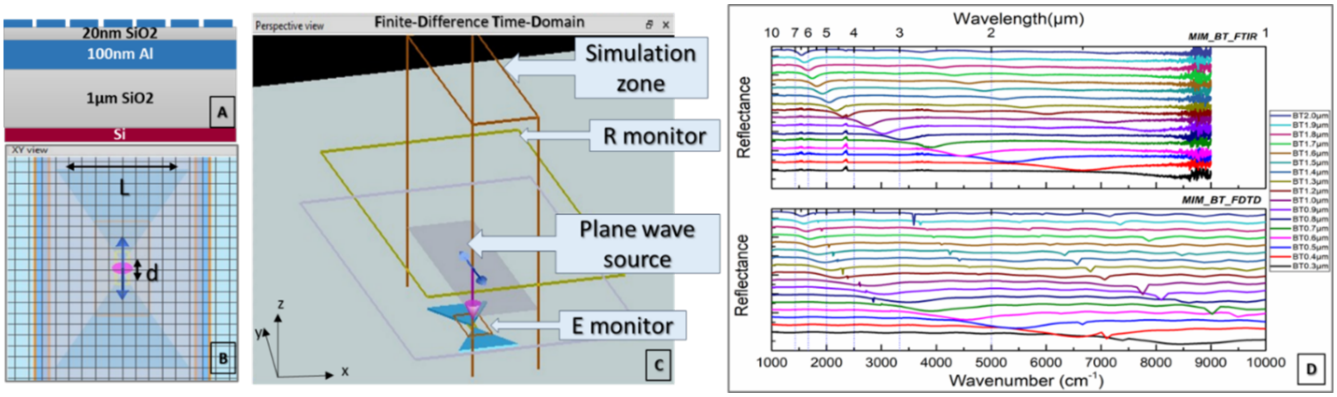


Fig. 1: A) Epitaxial layers from the substrate to the nano-structured Al-BT. B) XY top view from Lumerical simulation software. C) Perspective view of all simulation monitors wrapping up the Al-BT. D) FTIR measurement and Lumerial simulation results ofall Al-BTs array sizes.

References

[1] B. Cerjan et al. ACS Photonics 3, 354–360 (2016)
[2] B. Wang et al. Plasmonics 15, 609–621 (2020)
[3] F. B. Barho et al. Nanophotonics, 7, 507–516 (2017)

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Notes

TERS Characterization of Functionalized Gold Nanostructures for Nano-scale Biosensing

A. Tempez[1], J-F. Bryche[2,3], M. Vega[2,3,4], T. Brulé[1], T. Carlier[1], J. Moreau[4], P. Charette[2,3], M. Canva[2,3], and M. Chaigneau[1]

[1] *Horiba FRANCE SAS, Palaiseau, France*
[2] *Laboratoire Nanotechnologies et Nanosystèmes, IRL 3463 – CNRS, Université de Sherbrooke, Sherbrooke, Canada*
[3] *Institut Interdisciplinaire d'Innovations Technologiques 3IT – Université de Sherbrooke, Sherbrooke, Canada*
[4] *Laboratoire Charles Fabry - Institut d'Optique Graduate School, Université Paris-Saclay, CNRS, Palaiseau, France*

E-mail: `agnes.tempez@horiba.com`

Plasmonic gold nanostructures, through their ability to confine electromagnetic fields far beyond the diffraction limit, improve biosensor performance towards single-molecule detection in surface-enhanced Raman spectroscopy (SERS)[1]. Tip-Enhanced Raman Spectroscopy (TERS) characterization is a powerful analytical technique providing high chemical sensitivity for surface molecular mapping with nanoscale spatial resolution, which is useful to design highly sensitive and high-resolution biosensing structures. In this work, we studied with TERS experiments, functionalized gold nanodisk arrays on a gold-coated glass substrate that have recently shown good SERS performance[2] upon coupled plasmonic modes. The gold layer sustains propagative surface plasmons while the nanostructures sustain localized surface plasmon resonances. Coupling between them can occur in specific conditions and give rise to hybrid modes[3]. Nano-resolved TERS response distribution from grafted thiophenol molecules on nanodisks of 110 and 220 nm diameter feature strong signal localization on the periphery of the nanostructures, in agreement with numerical modeling[4]. This highlights the importance of grafting molecules on high electric field locations to optimize detection sensitivity and speed at low molecular concentrations.

References

[1] A. Bhattarai, K. T. Crampton, A. G. Joly, L. Kovarik, W. P. Hess, P. Z. El-Khoury, J. Phys. Chem. Lett., vol. 9, no. 24, 7105 (2018).

[2] J.-F. Bryche, R. Gillibert, G. Barbillon, P. Gogol, J. Moreau, M. Lamy de la Chapelle, B. Bartenlian, M. Canva, Plasmonics, vol. 11, no. 2, 601 (2015).

[3] M. Sarkar, M. Besbes, J. Moreau, J.-F. Bryche, A. Olivéro, G. Barbillon, A.-L. Coutrot, B. Bartenlian, M. Canva, ACS Photonics, vol. 2, no. 2, 237(2015).

[4] J.-F. Bryche, M. Vega, A. Tempez, T. Brulé, T. Carlier, J. Moreau, M. Chaigneau, P. G. Charette, M. Canva, Submitted to Nanomaterials (2021).

Notes

Photogenerated metasurface-based THz Modulator

J. Guise[1], S. Blin[1], E. Centeno[2], and T. Taliercio[1]

[1]*Institut d'Electronique et des Systèmes, Montpellier, France*
[2]*Institut Pascal, Clermont-Ferrand, France*

E-mail: `julien.guise@umontpellier.fr`

In the perspective of filling the lack of THz modulators, previous works have shown the possibility to optically modulate a THz beam crossing an InAs slab[1]. In the continuity of this work, we seek to reduce the required optical power by operating at 1550 nm in order to benefit from the fiber optic technology and to have a better control of the IR beam. Indeed, we show that to work at low power it is necessary to decrease the size of the IR beam to reach very high optical densities and we can thus generate many free carriers in the semiconductor by optical absorption process. The presence of these carriers allows to reach a quasi-metallic effect of the slab inthe desired THz range. We can then modulate the transmission of the THz wave crossing the modulator by switching it from an optically unpumped state (dielectric that transmits the THz wave) to an optically pumped state (metal reflecting the THz).

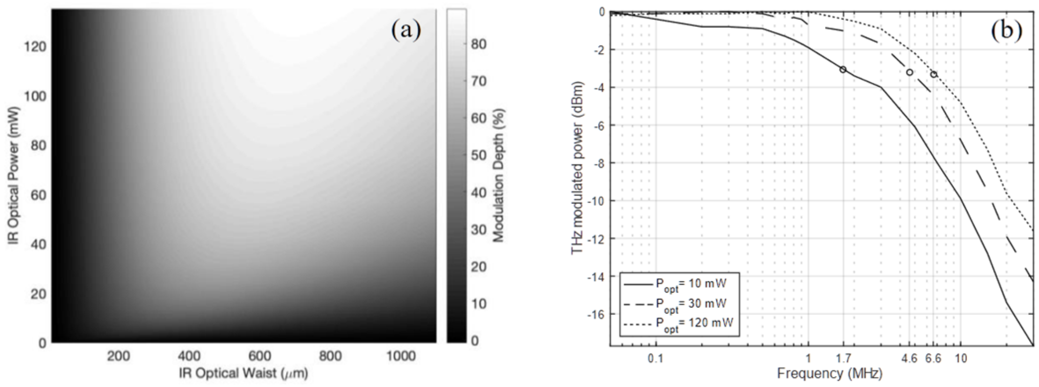

Fig. 1: (a) map of the THz transmission modulation ofa 5 µm-thick InAs slab for different IR waists (w_{opt}) and IR powers at THz waist (w_{THz}) = 550 µm (b) Experimental Bode for three IR powers with cutoff frequencies.

As shown in Fig. 1 (a) the MATLAB modelshows that using $w_{\mathrm{THz}} = 550\mu\mathrm{m}$ one can achieve up to 90% static modulation in the available IR power range. This optimum is reached when $w_{\mathrm{opt}} \approx w_{\mathrm{THz}}$ (optimal beam overlap). Using this optimal configuration, we perform the dynamic study of the modulation by plottingthe Bode diagrams in (b). It is then shown that when the IR optical power increases, the cutoff frequency increases. Indeed, since the density of photogenerated carriers increases, their lifetime decreases due to the Auger process and the modulator has a faster response.

References

[1] E. Alvear et al. Appl. Phys. Lett. 117, 111101 (2020)

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Notes

Nonlinear plasmonic cavities for Boolean calculations

F. Dell'Ova[1,2], R. Al Rafrafin[1], A. Cuche[2], C. Girard[2], Y. Brûlé[1], G. Colas des Francs[1], E. Raad[3], A. Berthaux[3], O. Narsis[3], C. Nicolle[3], E. Dujardin[2], and A. Bouhelier[1]

[1] *ICB laboratoire Interdisciplinaire Carnot de Bourgogne, CNRS UMR 6303, Université de Bourgogne Franche-Comté, 21078 Dijon, France*
[2] *CEMES Centre d'Élaboration de Matériaux et d'Études Structurales, CNRS UPR 8011, 31055 Toulouse, France*
[3] *CIAD laboratoire Connaissance et Intelligence Artificielle Distribuées, Université de Bourgogne Franche-Comté, 21078 Dijon, France*

E-mail: `florian.dell-ova@u-bourgogne.fr`

Plasmonic devices are promising solutions for optical information processing[1]. Here, we propose a two-dimensional double hexagon plasmonic cavity able to achieve Boolean calculations. These structures are made of crystalline gold using a focus ion beam etching technique. The high number of modes sustained by micrometric size cavities[2], makes this all-optical device a great reconfigurable tool, therefore allowing several Boolean functions with a single cavity. The inputs and outputs, $\mathrm{I_n}$ and $\mathrm{O_n}$, are defined by the apices of the cavity and are linked by the underlying modes[3]. We use two tightly focused laser pulses, encoding the input Boolean values into their respective states, to address selectively two inputs of the 2-bits Boolean logic gate. The output Boolean function is extracted from the intensity changes of the delocalized nonlinear photoluminescence collected at the readout locations, which is a sensitive probe of the plasmon-induced local electric field. With this simple geometry, we are able to build the truth table of all 2-inputs basic logic functions. To increase the complexity of the calculation, we play with the coherent excitation of the modes into the cavity when pulses are temporally synchronized on their respective inputs. We obtained the detection of the X-OR logic gate on a spread area of our nonlinear plasmonic device.

References

[1] U. Kumar et al., 'Designing Plasmonic Eigenstates for Optical Signal Transmission in Planar Channel Devices', ACS Photonics, vol. 5, no. 6, pp. 2328–2335, Jun. 2018, doi: 10.1021/acsphotonics.8b00137.

[2] U. Kumar et al., 'Spectral Tuning of High Order Plasmonic Resonances in Multimodal Film-Coupled Crystalline Cavities', Adv. Opt. Mater., vol. 7, no. 11, p. 1801787, 2019, doi: https://doi.org/10.1002/adom.201801787.

[3] A. Agreda et al., 'Spatial Distribution of the Nonlinear Photoluminescence in Au Nanowires', ACS Photonics, vol. 6, no. 5, pp. 1240–1247, May 2019, doi: 10.1021/acsphotonics.9b00181

Notes

1: Photochromic control of the photoluminescence of an emitter placed at the apex of a metallic nanocone

Reegan Aruldoss[1], Anne-Laure Baudrion[1], and Pierre-Michel Adam[1]

[1]*Light, nanomaterials and nanotechnologies (L2n) laboratory, CNRS ERL 7004, Université de Technologie de Troyes (UTT), France*

E-mail: `reegan.aruldoss@utt.fr`

The control of the spontaneous emission of emitters using plasmonic structures, either to enhance or quench the photoluminescence, mainly depends on the spectral overlap between the emitter's emissions/absorption and the Localized Surface Plasmon Resonance of the plasmonic structures[1]. As photochromic molecules can reversibly change from a transparent state to a coloured one by absorbing respectively UV and visible radiations, they were considered as excellent optical switches[2]. Lamri et al[3] in 2019, has experimentally demonstrated an optical control of the QDs-metal nanoparticle coupled system leading to an optical switch between quenching and enhancement of QD photoluminescence. However, the enhancement factor of this previous system was not optimized as many QDs were placed randomly on top of an array of silver nanocylinders. But herein, we propose to use nanocones, as they are capable of dramatically increasing the quantum efficiency of emitters placed at the tip[4]. We use here FDTD simulations to show an approximate 10 folds enhancement in the Purcell factor of an emitter placed at the apex of a silver nanocone before and after the photochromic transition of a spiropyran molecule (Fig.1).

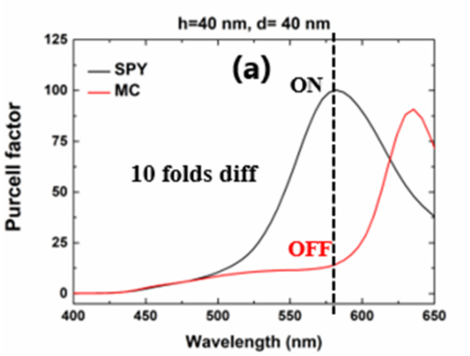


Figure 1: Purcell factors of a vertical dipole emitter placed at the tip of a silver nanocone and embedded in photochromic molecules. The nanocone height and base diameter are 70 nm and 40 nm respectively. The transparent state of the photochromic molecule is called Spiropyran (black curve) and the colored form is called Merocyanine (red curve).

References

[1] Viste, P. et al., ACS Nano 4 (2), 759-764 (2010)

[2] Photon-working switches, Yasuki Yokoyama, Keitaro Nakatani, editors - Springer, 2017

[3] Lamri, G. et al., Nanoscale 11, 258-265 (2019)

[4] Matsuzaki, K. et al., Scientific report 7, 42307 (2017)

2: Gold nanotriangles as a potential substrate for surface enhanced Raman spectroscopy (SERS) and biosensor

Fabrice Asonkeng[1,2], Julien Proust[1], Abdelhamid Hmima[1], Gaël Maranzana[2], and Thomas Maurer[1]

[1] *Laboratory Light, nanomaterials & nanotechnologies – L2n, University of Technology of Troyes & CNRS ERL 7004, 12 rue Marie Curie, 10000 Troyes, France.*

[2] *Université de Lorraine, CNRS, LEMTA, UMR 7563, 54504 Vandoeuvre Les Nancy, France.*

E-mail: `fabrice.asonkeng@utt.fr`

Until now, the prospects in terms of applications of gold nanotriangles (GNT) have been hindered due to the complexity of their synthesis process, which generally requires more than two steps before reaching at the geometry desired[1]. However, the optical properties of metallic nanoparticles, in particular gold nanoparticles, are highly dependent on their size and shape, and also on their organization. Especially for particles of triangular shapes, the properties vary the most depending on the edges of the vertices and the heights of the triangles. Thus, we have developed from recent work[2] a chemical synthesis method which makes it possible to manufacture GNT on the surface of various substrates. GNT are organized on the surface by self-assembly. This synthesis process consists essentially in dissolving in the same PGMEA (Propylene Glycol Monomethyl) solvent a metallic precursor of gold ($HAuCl_4$) and a homopolymer of PMMA (Polymethymetacrylate). GNT are created in real time on the surface of the substrate under specific annealing conditions. The manufactured nanostructures exhibit an interesting plasmonic activity. For this, the latter can be used as potential components of plasmonic sensor types, in particular SERS (Surface-Exalted Raman Scattering) sensors to improve their sensitivity.

A first test was done, GNT have been used as a SERS substrate to identify the Raman spectra of a non-resonant probe molecule called trans-1,2-bis-(4-pyridyl)-ethene (BPE) at different concentrations. This original process allows us to detect traces of BPE down to nanometric concentrations.

This original, rapid and less expensive single-step synthesis process is also a promising way for heterogeneous catalysis applications such as the fabrication of gold nanotriangles catalysts for CO_2 reduction.

References

[1] Scarabelli, L et al., ACS Nano 2014, 8 (6), 5833–5842.

[2] Sarrazin, A et al., Nanotechnology 2014, 25 (22), 225603.

3: Étude comparative de la sensibilité SERS de substrats commerciaux

A. Azziz[1], W.Safar[1], M. Edely[1], and Marc Lamy de la Chapelle[1]

[1]*Institut des Molécules et Matériaux du Mans - UMR 6283 CNRS Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans, Cedex 9, France*

E-mail: `marc.lamydelachapelle@univ-lemans.fr`

Depuis 1974 et l'observation par Fleischman de l'exaltation du signal Raman de la pyridine lorsque celle-ci était au contact d'une electrode d'argent rugueuse[1], de nombreux efforts ont été déployés pour comprendre, contrôler et tirer parti de la diffusion Raman exaltée de surface (SERS en anglais). Il a ainsi été établi qu'une part importante de l'exaltation du signal Raman provenait de l'augmentation du champ électromagnétique au voisinage de la surface métallique. L'interaction entre la lumière incidente et les nanostructures métalliques induit l'excitation de plasmons de surface localisés renforçant ainsi le champ électromagnétique local.

Depuis qu'il a été démontré en 1997[2] que la technique était capable de détecter une molecule unique, son application à la détection analytique s'est considérablement développée. De nombreux groupes de recherche ont ainsi développé plusieurs méthodes pour produire des capteurs SERS tels que des solution colloidales de nanoparticules d'or et d'argent colloïdales. Bien que ces systèmes aient démontré leur facilité d'utilisation et leur fort effet d'exaltation, ils sont limités par un manque de reproductibilité dû à l'agrégation indésirable des colloïdes métalliques dans les matrices aqueuses et biologiques.

Par rapport aux nanoparticules, les substrats SERS basés sur des nanoréseaux métalliques supportés sont des structures hautement stables et ordonnées à longue portée.

Dans la continuité de nos travaux précédents sur la reproductibilité de substrats SERS commerciaux[3], nous avons comparé les performances analytiques de trois substrats SERS disponibles dans le commerce: Hamamatsu, Q-SERS et RAM-SERS-SP. Des mesures de sensibilité ont été réalisées avec des solutions de concentrations croissantes d'acide 4-mercaptobenzoïque (MBA).

References

[1] Fleischmann, M., Hendra, P. J. & McQuillan, A. J., Chemical Physics Letters 26, 163 (1974).

[2] Kneipp, K. et al., Physical review letters 78, 1667 (1997).

[3] Y. Liu et al., Plasmonics, 15, 743 (2019)

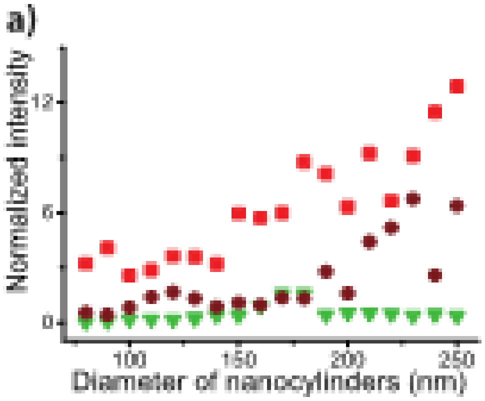
4: Gold Nanocylinders on Gold Film as a Multi-spectral SERS Substrate

W. Safar[1], M. Lequeux[2], J. Solard[3], A. P. A. Fischer[3], N. Felidj[4], P. G. Gucciardi[5], M. Edely[1], and M. Lamy de la Chapelle[1]

[1] *IMMM - UMR 6283 CNRS, Le Mans Université, 72085 Le Mans, Cedex 9, France*
[2] *Université Paris 13, Laboratoire CSPBAT, CNRS, (UMR 7244), 93017 Bobigny, France*
[3] *Université Paris 13, Laboratoire de Physique des Lasers, CNRS, (UMR 7538), 93050 Villetaneuse, France*
[4] *Université Paris 13, ITODYS, CNRS, UMR 7086, F-75013 Paris, France*
[5] *CNRS IPCF, Instituto per i Processi Chimico-Fisici, I-98158 Messina, Italy*

E-mail: `wafasafar@hotmail.com, marc.lamydelachapelle@univ-lemans.fr`

The surface enhanced Raman scattering (SERS) efficiency of gold nanocylinders deposited on gold thin film is studied. Exploiting the specific plasmonic properties of such substrates, we determine the influence of the nanocylinder diameter and the film thickness on the SERS signal at three different excitation wavelengths (532, 638 and 785 nm). We demonstrate that the highest signal is reached for the highest diameter of 250 nm due to coupling between the nanocylinders and for the lowest thickness (20 nm) as the excited plasmon is created at the interface between the gold and glass substrate. Moreover, even if we show that the highest SERS efficiency is obtained for an excitation wavelength of 638 nm, a large SERS signal can be obtained at all excitation wavelengths and on a wide spectral range. We demonstrate that it can be related with the nature of the plasmon (propagative plasmon excited through the nanocylinder grating) and with its angular dependence (tuning of the plasmon position with the excitation angle). Such an effect allows the excitation of plasmon on nearly the whole visible range, and paves the way to multispectral SERS substrates[1].



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

References

[1] W. Safar, M. Lequeux, J. Solard, A. P. A. Fischer, N. Felidj, P. G. Gucciardi, M. Edely, M. L. de la Chapelle, Nanomaterials, 10(5), 927, (2020).

5: Relation propriétés optiques / propriétés thermiques de nanostructures métalliques

C. Naveau[1], M. Edely[1], G. Vaudel[1], R. Ruello[1], and Marc Lamy de la Chapelle[1]

[1] *Institut des Molécules et Matériaux du Mans - UMR 6283 CNRS Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans, Cedex 9, France*

E-mail: `marc.lamydelachapelle@univ-lemans.fr`

Les nanostructures métalliques présentent des propriétés spécifiques liées à leur forme et à leur taille nanoscopique. Dans ces conditions particulières, les propriétés de la matière qu'elles soient électroniques, optiques, thermiques ou mécaniques... sont très différentes des propriétés à l'échelle macroscopique. On observe alors des modifications notables qui peuvent être exploitées dans de nombreuses applications telles que les capteurs, les spectroscopies ou la synthèse de molécules...

L'objectif de ce travail est d'étudier les propriétés optiques des nanoparticules métalliques et de déterminer leur lien avec leurs propriétés thermiques[1-4]. En effet, lors de l'excitation de nanoparticules par la lumière, il est possible d'induire l'oscillation collective des électrons, connue sous le nom de plasmon de surface localisée. Lors de ce processus, la lumière peut soit être absorbée soit être diffusée. Dans le premier cas, l'énergie optique est dans la plupart des cas transformée en chaleur provoquant une augmentation locale de la température.

Le but est alors de déterminer l'influence du plasmon de surface localisée sur les propriétés thermiques des nanoparticules en fonction de la taille des nanoparticules. Pour se faire, l'interaction lumière/nanoparticules est tout d'abord mesurée par absorption UV-visible pour déterminer la position de la résonance plasmon sur des nanoparticules sphériques colloïdales de 50 et 100 nm de diamètre. Dans un deuxième temps, l'élévation de température induite par une excitation laser est mesurée sur les solutions colloïdales. En balayant en longueur d'onde la gamme de visible, il est alors possible de relier la température de la solution à l'excitation plasmonique des nanoparticules.

References

[1] G. Baffou et al., Laser Photonics Rev. 7, 171 (2013)
[2] G. Picardi et al., J. Phys. Chem. C 120, 26025 (2016)
[3] H. Moustaoui et al., J. Phys. Chem. C 123, 17548 (2019)
[4] A. Campu et al., Nanotechnology 50, 405701 (2019)

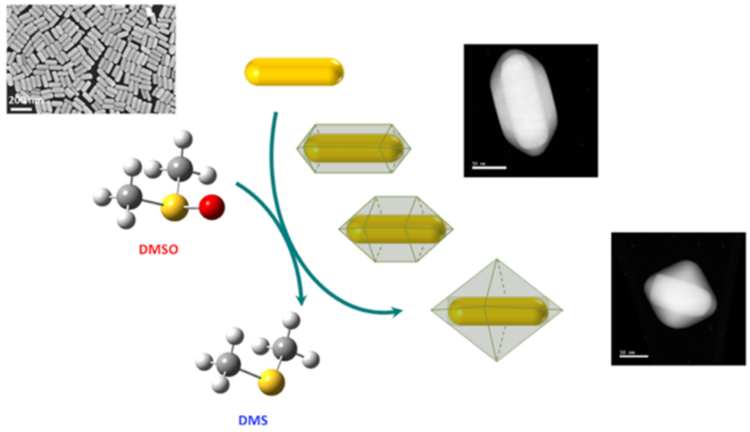
6: Symmetry Reduction in the Growth of Plasmonic Nanocrystals

I. Haidar[1], B. Morcos[1], M. Seydou[1], F. Maurel[1], P. Decorse[1], J. Nelayah[1], A. Chevillot-Biraud[1], S. Lau-Truong[1], J. Aubard[1], N. Félidj[1], and L. Boubekeur-Lecaque[1]

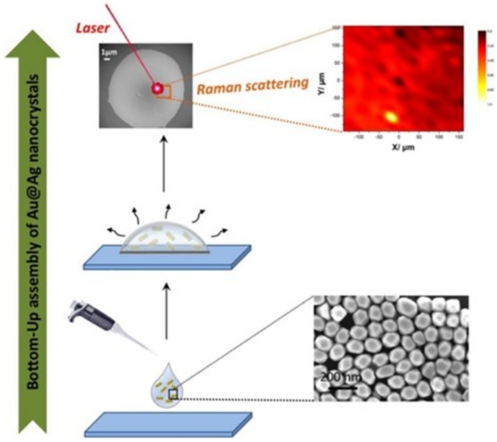
[1] *Laboratoire ITODYS UMR 7086, Université Paris Diderot, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France.*

E-mail: `leila.boubekeur@u-paris.fr`

The shape and size control of metal nanoparticle at the nanoscale is a crucial step in the development of diverse applications ranging from catalysis to plasmonics and surface-enhanced Raman spectroscopy (SERS). For seed-mediated growth of nanocrystals, it is well established that the final morphology is dictated not only by the crystallinity of the seed but also by surfactant and additives.[1] However, the systematic study of the impact and the fate of these additives to elucidate the growth mechanism remains challenging. We will show how the combination of surface enhanced Raman scattering and X-ray photoelectron spectroscopies revealed the key role played by DMSO in the synthesis of core-shell Au@Ag and its fate upon silver reduction.[2]



(a) Tailoring the Shape of Core-Shell Au@Ag Nanoparticles in Dimethyl Sulfoxide.



(b) Bottom-up assembly of Au@Ag plasmonic nanocrystals.

The core-shell Au@Ag nanoparticles obtained via this synthetic strategy tend to self-assemble on large area on solid substrate. Through a bottom-up approach, these densely packed nanoparticle films proved very promising SERS-active substrates in terms of homogeneity, stability over time and overall cost-effectiveness.[3]

References

[1] L. Polavarapu et al., CrystEngComm 2015, 17 (20), 3727-3762
[2] I. Haidar et al., Chem. Mat. 2019, 31, 2741-2749
[3] I. Haidar et al., Appl. Mat. Today 2019, 15, 462-471

7: Advanced anisotropic hybrid plasmonic nano-emitters

Minyu Chen[1], Dandan Ge[1], Sylvie Marguet[2], Ali Issa[1], Safi Jradi[1], Christophe Couteau[1], and Renaud Bachelot[1]

[1] *Light, Nanomaterials, Nanotechnologies (L2n) Laboratory, CNRS ERL 7004, University of Technology of Troyes, 12 rue Marie Curie, 10004 Troyes, Cedex, France.*

[2] *Université Paris Saclay, CEA, CNRS, NIMBE, 91191 Gif sur Yvette, France*

E-mail: `renaud.bachelot@utt.fr`

Hybrid nanomaterials are highly attractive by a rapidly growing group of nanooptics researchers, due to the promise in light control and effective methods for both fundamental studies and applications of the surface plasmon.[1,2] Hybrid plasmonic nanosources, generally formed by metal and other luminescent material connected at the nanometer scale, combine the surface plasmons of metal, light emission of emitters and additional properties due to synergistic effects between the components.[3]

Our work aimed at fabricating anisotropic hybrid plasmonic nano-emitters using near-field two-photon polymerization which is triggered by localized field enhancement from localized surface plasmons by metal nanoparticles.[1,2] By trapping the nano-emitters (QDs) inside the polymer or at its surface, location of the nano-emitters can be controlled by changing the spatial distribution of the polymer near the metal nanostructures. Furthermore, this hybrid plasmonic nanosource can be commanded by a simple polarized monochromatic beam and presents the unique specificity to be based on mixing of colors issued from an anisotropic hybrid nanostructure containing different quantum dots whose spatial distribution is anisotropic and controlled at the nanoscale. We will present recent achievements on this approach. (See Fig. 1)

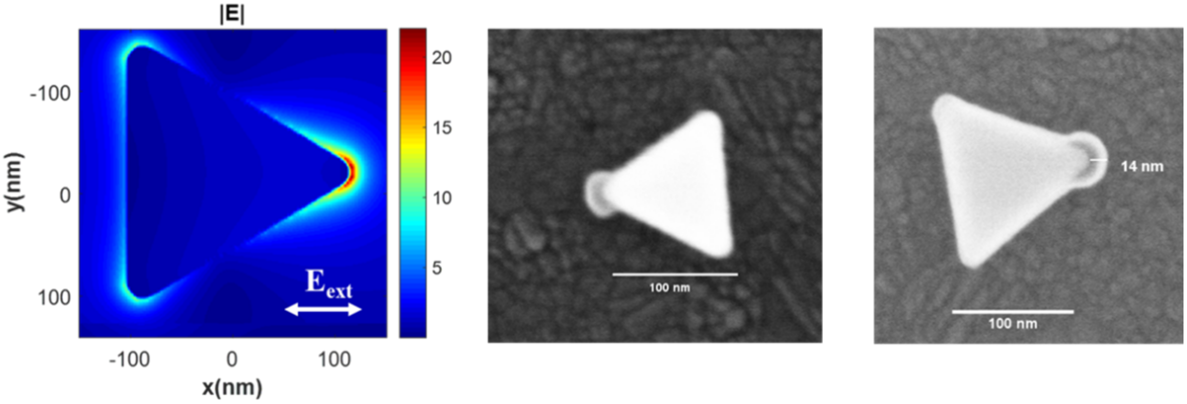


Figure 1: Left: FDTD Calculation of the optical properties of an Au triangle deposited on ITO-coated glass substrate; Middle and right: SEM images of hybrid plasmonic system.

References

[1] X. Zhou et al, Nano Letters 15, 7458 (2015)
[2] D. Ge et al, Nature Communications 11, 3413 (2020)
[3] G. Lamri et al, Nanoscale 11, 258 (2019)

8: Photopolymerization initiated by photochromic molecules in the context of the development of active plasmonic nano-sources

Dandan Ge[1], Erell Bodinier[1], Safi Jradi[1], and Anne-Laure Baudrion[1]

[1] *Light, nanomaterials, nanotechnologies (L2n), Université de technologie de Troyes, 12 Rue Marie Curie, 1000 Troyes, France*

E-mail: `anne_laure.baudrion@utt.fr`

Photochromic molecules (PMs) have attracted a lot of interest because of their reversible switch between a transparent and a colored state by absorbing UV/visible light. Recently, they have been used as an optical switch to control the coupling between plasmonic particles and quantum dots (QDs), switching from enhancement to quenching of the photoluminescence[1]. Moreover, during the same time, researchers of L2n demonstrated a method based on near-field nano-photopolymerization, that is triggered by localized surface plasmons resonance (LSPR) of metallic particles[2]. They trapped QDs in anisotropic distributed polymer lobes and thus created two-color emitters, which were sensitive to the polarization of the exciting light[3]. This gives a potentiality to create nanometric polymer lobes containing PMs, able to switch between plasmonic quenching and enhancement of the QDs' photoluminescence, at the single metallic nanoparticle level.

During the first attempt, we discovered that the PMs can be directly used as photoinitiator to achieve single-photon polymerization (SPP) and two-photon polymerization (TPP) to fabricate 1D, 2D and 3D microstructures. In addition, under the single-photon polymerization, the PMs trapped inside the polymer film maintains their photochromic properties after photopolymerization. We will show that spiropyran molecules displays a much higher efficiency for 2-photon polymerization than the well-known photoinitiator, Irgacure 819. After mixing the spiropyran molecules and Irgacure 819, their mixed efficiency shows a superposition effect rather than competition effect. The polymer film containing spiropyran molecules fabricated by SPP using white light exhibits photochromic reaction after UV irradiation and its recovery speed is studied in three ways, in dark, visible light irradiation and heating.

References

[1] Lamri G., et al., Nanoscale, 11(1), 258-265 (2019).

[2] Zhou, X., et al. ACS Photonics, 2 (1), 121–129 (2014).

[3] Zhou, X., et al., Nano Letters, 15 (11) 7458 – 7466 (2015).

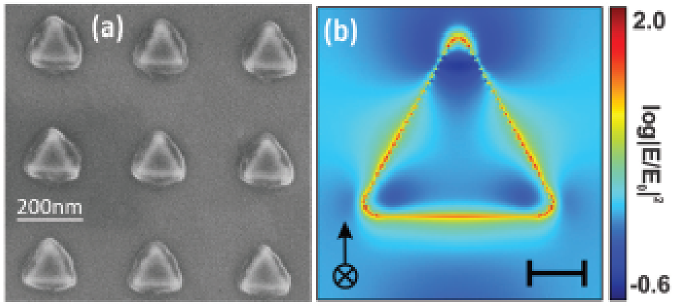
9: Extending nanoscale patterning with multipolar surface plasmon resonances

Issam Kherbouche[1,2], T. Geronimi Jourdain[1], Danielle McRae[3], Azzédine Lamouri[1], Leïla Boubekeur-Lecaque[1], François Lagugné Labarthet[3], Claire Mangeney[2], and Nordin Felidj[1]

[1] *Université de Paris, Laboratoire ITODYS, CNRS, F-75006 Paris, France*
[2] *University Paris 05, Lab Chim & Biochim Pharmacolog & Toxicol, 75006 Paris, (France)*
[3] *Department of Chemistry, University of Western Ontario, 1151 Richmond street, London, On, N6A 5B7, Canada*

E-mail: `nordin.felidj@univ-paris-diderot.fr`

Plasmon-driven surface functionalization of nanoparticles is receiving growing attention as it allows generating locally tailored chemical reactivity on the nanoparticle surface. The extension to surface multi-functionalization still represents a major breakthrough in chemistry[1]. In this talk, we address this issue by triggering regiospecific surface double-functionalization under plasmon excitation, using diazonium salts as surface functionalization agents. Lithographic gold nano-triangles, displaying multipolar plasmon modes, were selected to pattern the surface by two different types of functional poly(aryl) layers, bearing either carboxyl or hydroxyethyl pendant groups. This double-functionalization strategy is triggered by the wavelength of the incident light, matching the dipolar and quadrupolar plasmon modes respectively, leading to a site-selective hot-electrons mediated reduction of aryl diazonium salts[2]. The grafting occurs specifically in the regions of maximum of field enhancement, leaving the other areas of the nanostructure chemically passive. We believe that this plasmonic-based approach will not only pave a new way for the multi- functionalization of plasmonic nanoparticles but also provide a general strategy to attach molecules to hot spot regions and further improve their SERS detection and analysis for (bio) sensing applications.



(a) SEM image of the triangles (array A), after immersion in an aqueous solution of diazonium salt (3 mM) and optical exposure at 633 nm for a polarization along the Y axis; (b) mapping of the intensity of the incident electric field at 600 nm, calculated by the FDTD method for a triangular target with 170 nm side length, height 50 nm, and a grating constant of 340 nm (polarization along the Y axis).

References

[1] I. Tijunelyte, et al., Nanoscale Horizon, 2018, 3, 53-57.
[2] I. Kherbouche, et al, Nanoscale (https://doi.org/10.1039/D1NR02181H, June 2021).

10: Joint determination of thicknesses and optical properties of copper/oxide nanolayers

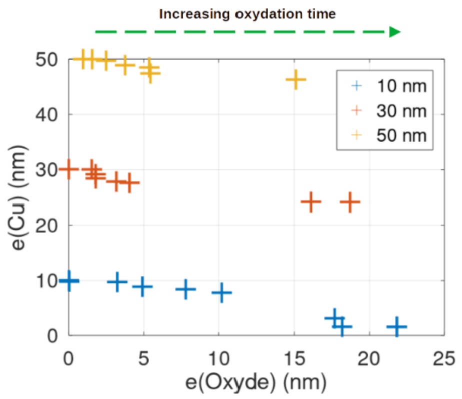
T. Gharbi[1,2] and D. Barchiesi[1]

[1] *Group for Automatic Mesh Generation and Advanced Methods, University of Technology of Troyes, 12 rueMarie Curie, CS 42060, F-10004 Troyes Cedex, France*

[2] *Georesources Materials Environment and Global Changes Laboratory (GEOGLOB), Faculty of Sciencesof Sfax, University of Sfax, 3018, Sfax-Tunisia, Tunisia*

E-mail: `tasnim.gharbi@utt.fr`

Nanolayers based materials are considered powerful, exceptional and interesting uses in several advanced technological applications mostly in optical engineering field. The most used materials are the noble metals but also Copper and various alloys. At nanometric scale, their material structure related to the mode of deposition and to the annealing of samples, as well as the confinement of free electrons, are known to modify their optical properties[1]. On the other hand, to model and optimize the nanostructures, or even to better match the modeling results and the experimental results, especially for resonant structures, a realistic fitting of the optical properties is of great interest. To avoid the use of the optical properties of the bulk materials to determine the thicknesses and that of the thicknesses to determine the optical properties, as done in ellipsometry, we propose a method for recovering both the thicknesses and the fitting parameters of the optical properties from absorbance curves. In this study, we use both a multilayer electromagnetic model and partial fractions models to describe a Copper/Copper oxide bilayer. We solve the inverse problem with hybrid metaheuristic direct approaches (evolutionary, artificial bees and particle swarm methods with Nelder-Mead based end of descent). The multi-objective approach is expected to avoid the risk of non-unicity[2].



References

[1] D. Rioux, PhD thesis, École Polytechnique de Montréal (2015) – H. Ditlbacher et al. Physical Review Letters. 95257403 (2006) – T. Larocheet al. Appl. Phys. Lett. 91 123101 (2007) – D. Skiginet al. Applied Optics, 56, (7) 1807(2017)

[2] D. Barchiesiet al. Journal of Nanophotonics, 8,(1) 083097(2014), D. Barchiesi et al. Optical Materials 91138 (2019)

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11: Nanorod Assembly Driven by Liquid Crystal Topological Defects

Haifa, Jeridi[1], Loup Chopplet[1], Bruno Gallas[1], Cyrille Hamon[2], Emmanuel Lhuillier[1], and Emmanuelle Lacaze[1]

[1] *CNRS-Sorbonne université, Institut des Nano-Sciences de Paris (INSP)*
[2] *Laboratoire de Physique des Solides, Bat.510, UMR-CNRS 8502, Université Paris-Sud, Université Paris-Saclay, F-91405 Orsay, France*

E-mail: `emmanuelle.lacaze@insp.jussieu.fr`

It has been shown that advanced hierarchical structures of liquid crystal topological defects can be used to confine gold nanospheres (NP) and sequentially transfer their geometrical features to the NP organizations[1]. We use two kinds of liquid crystal topological defects, 1D dislocations and 2D ribbon-like grain boundaries, forming organized arrays of oriented defects embedded in the same liquid crystal smectic films[2]. We showed their ability to confine NPs, either in 1D or in 2D. In the 1D defects, NP chains are formed; in the 2D defects 2D hexagonal networks of NPs are formed[1]. We now show how such an ordering ability transfer to nanorod (NR) organizations.

We have used fluorescent NRs (CdSe/CdS nanorods of diameter 7nm and length 22nm) that have been probed by fluorescent microscopy. We observe that NRs are perfectly oriented in chains within the 1D defects[3]. NR ribbons are formed at higher concentration, confined in the 2D topological defects. We demonstrate that even for ribbons as large as some hundreds of nanometers, the average NR orientation, whatever slightly less defined than for chains in 1D defects, remains well-controlled, along one single orientation, the defect orientation. For the highest possible NR concentrations this leads to a large number of NR ribbons longer than 10µm, with polarization of emission fixed along one single direction.

We also study how such an orienting behavior applies to gold nanorods (diameter 10nm) and nano-bipyramids (diameter 15nm). We again obtain formation of NR ribbons. A highly anisotropic plasmon absorption fully controlled by light polarization demonstrates the efficiency of the 2D defects-induced orientation of the NRs organized inribbons. In addition, by monitoring the liquid crystal topological defect nature we show that only one kind of defect is able to provide anisotropic plasmon absorption in direct relation with the intimate structure of the corresponding liquid crystal grain boundary.

References

[1] S.P. Do et al., Nano Letters (2020)
[2] D. Coursault et al., Soft Matter (2016)
[3] L. Pelliseret al., Adv. Funct. Mat. (2015)

12: SPR bio-sensors to probe the DNA-pesticides interactions

Sarabjeet Kaur[1], Julien Vaillant[1], Aurélien Bruyant[1], Safi Jradi[1], and Julien Proust[1]

[1] *Laboratory of Light, Nanomaterials and Nanotechnologies (L2n), CNRS ERL 7004, University of Technology of Troyes, Troyes, France*

E-mail: `julien.proust@utt.fr`

The framework of our study revolves around the development of Surface Plasmon Resonance (SPR) based DNA biosensor that is dedicated to detecting the changes in DNA when toxic molecules will interact with it. Noble-metal gold (Au) is a crucial part of our research as we employ it as a surface transducer due to its extraordinary electrochemical, optical and biocompatible properties. The interaction of toxic molecules with human DNA creates mutations and translocations, causing chronic diseases such as cancer. The primary emphasis of the study is to focus on the plasmonic response of the Au sensor layer bound with thiolated ssDNA and then hybridized with Gold Nanoparticle (AuNP) functionalized cDNA. This combination of dsDNA with Au film on one side and AuNP on the other acts as a receptor layer for toxic molecules (as in Fig 1). Changes occurring in the vicinity of metallic layer upon the interaction of receptor layer with toxic molecules modifies the refractive index which induces a shift in resonance angle and hence blue/red shift in resonance curve (an experimental example in Fig 2).

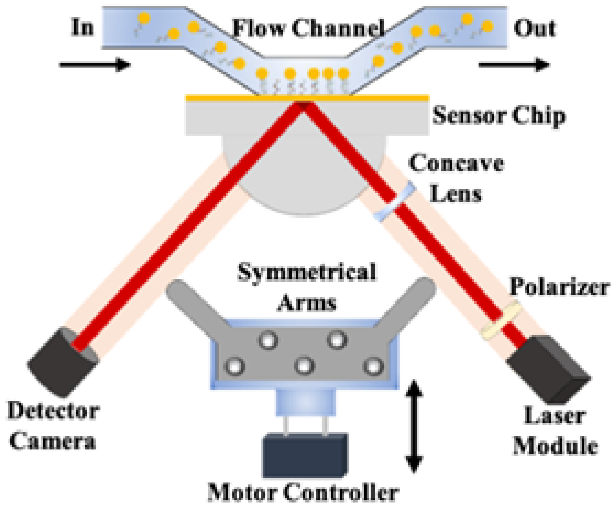


Fig 1: Schematic representing SPR setup

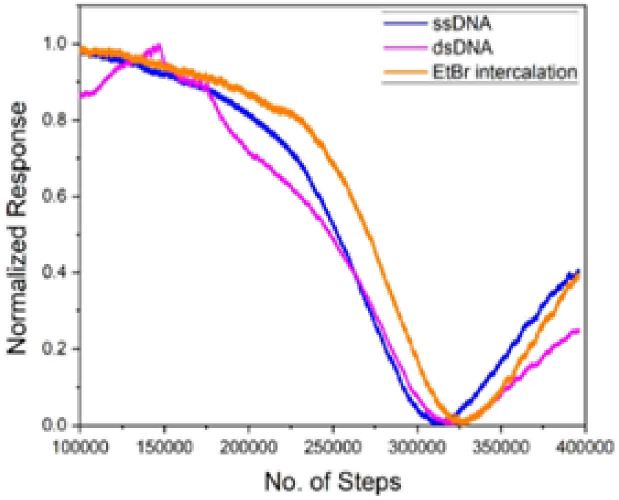


Fig 2: Sensograms detecting Ethidium bromide

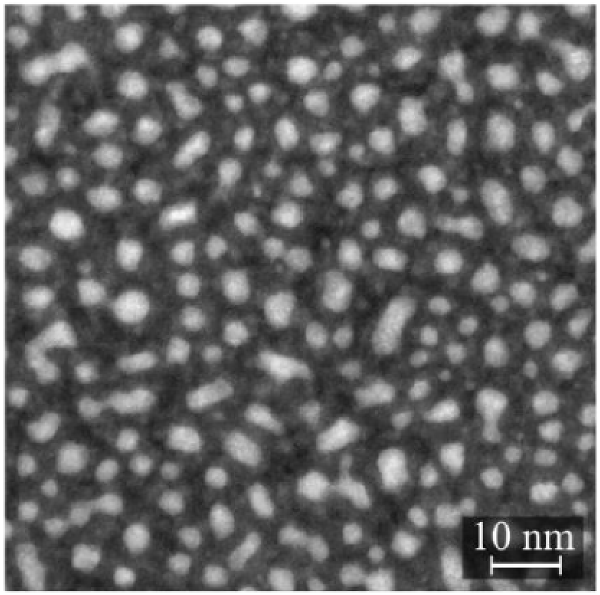
13: Optical properties of monolayer of nanoparticles in a thin-film stack

M.C. Solignac[1,2], H. Montigaud[1], M. Balestrieri[1], I. Gozhyk[1], K. Vynck[2], and P. Lalanne[2]

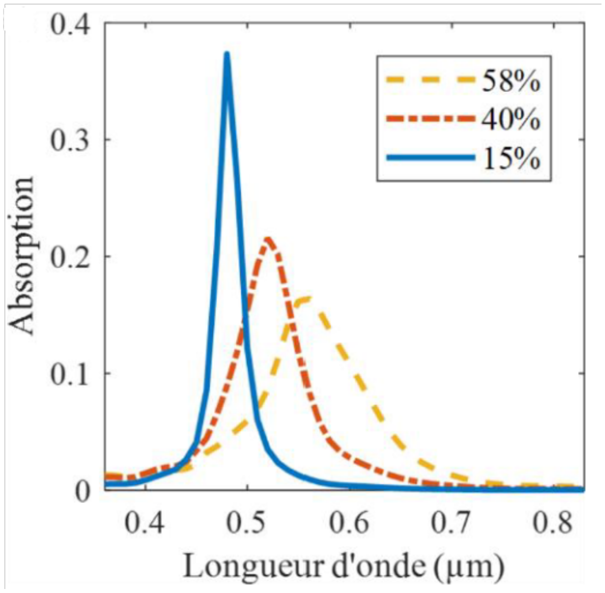
[1] *Surface du Verre et Interfaces UMR 125 CNRS/Saint-Gobain, Aubervilliers, France*
[2] *LP2N, CNRS, Institut d'Optique Graduate School, Univ. Bordeaux, 33400 Talence, France*

E-mail: `marie-caroline.solignac@saint-gobain.com`

In the present work, we investigate experimentally and theoretically the optical properties of thin-film stacks containing monolayer of silver nanoparticles. The nanoparticles are grown directly on the surface by magnetron sputtering deposition. They have a spheroidal truncated shape of diameter 1-10 nm and are distributed randomly on a dielectric substrate (Figure (a)). Effective medium theories[1,2] are often used to describe the optical properties of such system. However, they don't take well into account interaction between particles at high surface coverage. With different tools[3,4], we studied the effect of density of particles on the optical properties. Results shown in Figure (b) highlights the importance of interaction between particles.



(a) STEM-HAADF plane-view image of Ag nanoparticles (light grey) encapsulated in a dielectric.



(b) Calculated absorption spectra for a monolayer of Ag nanoparticles(spherical, same size) at surface coveragerate.

References

[1] J.C. Maxwell-Garnett, Phil. Trans. Roy. Soc205, 237(1906)
[2] A. Reyes-Coronado, OpticsExpress26, 12660(2018)
[3] M. Bertrand, J Opt Soc Am A 37, 70 (2020)
[4] R. Lazzari, Thin Solid Films 419, 124 (2002)

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