

**GROUPEMENT DE RECHERCHES 3430
PLASMONIQUE MOLECULAIRE, SPECTROSCOPIES EXALTEES**

Journées plénières les lundi 2 et mardi 3 Juin 2014 – Université Paris Diderot

Chers collègues,

Les prochaines journées plénières du GDR PMSE auront lieu les Lundi 2 et Mardi 3 juin 2014, sur le campus de l'Université Paris Diderot (**amphithéâtre Pierre-Gilles de Gennes, bâtiment Condorcet**).

Ces deux journées seront l'occasion de faire le point sur les avancées scientifiques des groupes de recherches par le biais de présentations orales, de posters et de discussions. Cinq conférences plénières seront au programme:

- **François LAGUGNE-LABARTHET**, Western University, Canada: "Plasmonique et spectroscopie : Comment accroître la sensibilité et la résolution spatiale de mesures locales ?";
- **Christian HUCK**, KIP, Heidelberg University, Allemagne: "Antenna enhanced vibrational spectroscopy";
- **Emmanuel FORT**, Institut Langevin, ESPCI, Paris : « plasmonique moléculaire »
- **Pietro GUCCIARDI**, IPCF-CNR, Messine (Italie): How a nanoantenna modifies the polarization state of the SERS Photons?
- **Adnen MLAYAH**, laboratoire CEMES, Toulouse : « Metal nanoparticle environment probed using SERS blinking »

Les journées plénières sont soutenues par le Labex SEAM « Science and Engineering for Advanced Materials and devices » (<http://www.labex-seam.fr/>).

Vous trouverez ci-dessous le programme des journées, les résumés des présentations et la liste des participants.

Bien cordialement,

Marc Lamy de la Chapelle / Nordin Félidj
(Site web: <http://www.univ-paris13.fr/gdrpmse/gdrpmse3430@gmail.com>)

PROGRAMME SCIENTIFIQUE – Journées GDR PMSE (2 et 3 Juin 2014)

	8h30	Accueil des participants
<u>02/06/2014</u>	9h00	Introduction aux journées plénières (Marc Lamy de la Chapelle, Nordin Félidj)
	9h10-12h00	Session SERS (chairman : Nordin Félidj) 9h10-9h50 : Pietro GUCCIARDI. Conférence plénière : How a nanoantenna modifies the polarization state of the SERS Photons ? 9h50-10h10 : Alexa COURTY : Auto-organisations de Nanoparticules d'Argent : application pour la diffusion Raman Exaltée de Surface. 10h10-10h30: Israa HAIDAR: Assemblages de nanoparticules en dimères pour la Spectroscopie Raman Exaltée de Surface Pause-café: 10h30 – 11h00 Session SERS (chairman : Pietro Gucciardi) 11h-11h20 : Mitradeep SARKAR : Exaltation de champ en utilisant de nouveaux modes plasmoniques : couplage entre des plasmons localisés de nanoparticules et les plasmons propagatifs d'un film métallique. 11h20-11h40: Dominique BARCHIESI : Points chauds autour d'une nanoparticule. 11h40-12h00 : Florent COLAS : Near-field to far-field considerations of SERS measurements on nanocylinders in a periodic arrangement.
	12h00-13h30	Pause repas
	13h30-14h50	Session TERS (chairman : Jean-Christophe Valmalette) 13h30-14h10 : François LAGUGNE-LABARTHET : “Plasmonique et spectroscopie : Comment accroître la sensibilité et la résolution spatiale de mesures locales ?” 14h10-14h30: Marc CHAIGNEAU: Billion Fold Increase in Tip Enhanced Raman Signal 14h30-14h50: Angéline D'ORLANDO: Un couplage AFM-Raman pour élaborer des nanostructures métalliques exaltantes du spectre Raman, sans contact chimique entre molécules et métal.
	14h50-15h50	Pause-café / Poster
	15h50-17h30	Session Plasmonique moléculaire (chairman : Jean Aubard) 15h50-16h30 : Adnen MLAYAH. Conférence plénière: « Metal nanoparticle environment probed using SERS blinking » 16h30-16h50 : Mai Tuyet NGUYEN: Lithographic Gold@Polymer Nanorods

		as Efficient Thermoswitchable Plasmonic Systems for Environmental Sensing Applications <i>16h50-17h10 : Delphine SHAMMING: Electrochemically tunable plasmon resonance of gold nanoparticles functionalized by covalently grafted oligomers or by deposited conducting polymers</i> <i>17h10-17h30 : Andrey ARISTOV: Phase-sensitive plasmonic metamaterials for biosensing</i>
<u>03/06/2014</u>	9h00 : Accueil des participants	
	9h15-12h40	Session spectroscopies exaltées de surface (chairman : Bernard Humbert) <i>9h10-9h50 : Christian HUCK. Conférence plénière: “Antenna enhanced vibrational spectroscopy”</i> <i>9h50-10h10 : Petru GHEMUCHE : Plasmonic enhanced fluorescence energy transfer</i> <i>10h10-10h30 : Céline FIORINI : Etude des propriétés de luminescence à 2 photons de nano- bâtonnets d’or colloïdaux uniques</i> - Pause-café : 10h30 – 11h00 Session applications (chairman : Emmanuel Rinnert) <i>11h00-11h40 : Emmanuel FORT. Conférence plénière: »plasmonique moléculaire «</i> <i>11h40-12h00 : Alexandre MERLEN : La molécule d’aminothiophenol en spectroscopie Raman exaltée de surface</i> <i>12h00-12h20 : Inga TIJUNELYTE : Nano-plasmonics tuned “click chemistry” monitored in situ by Surface Enhanced Raman Spectroscopy</i> <i>12h20-12h40 : Valérie STAMBOULI : TiO₂-Ag^o plasmonic sensor for the SERS detection of organic molecules.</i>
	12h40-12h50	Conclusion des journées plénières (Marc Lamy de la Chapelle, Nordin Félidj)

RESUMES – CONFERENCES INVITEES

How a nanoantenna modifies the polarization state of the SERS Photons?

P. G. Gucciardi, IPCF-CNR, Messine (Italie)

Photons generated in Surface Enhanced Raman Scattering (SERS) from rough metal substrates are generally unpolarized due to the random orientation of the molecules and of the nanostructures. Ordered nanoantennas, such as metallic dimers and nanorods arrays have highlighted a strong intensity dependence of the SERS intensity on the polarization of the excitation field. Here we show that SERS from randomly oriented molecules, adsorbed on self-assembled gold near-field coupled nanowires is strongly polarized along the wire-to-wire nanocavity axis. Experiments on individual nanoantennas featuring two distinct local surface plasmons show that the polarization of the SERS photons is strongly dependent on the pump field wavelength and its capability to resonantly excite the specific nanoantenna localized plasmon resonance (LSPR). A 90° polarization rotation is found when excitation is resonant with either with the long or the short axis LSPR. Experiments with circularly polarized light evidence the peculiar effect of the density of photons states inside resonant nanocavities to polarize the re-radiated SERS photons. Finally a theoretical model is illustrated, providing the exact laws ruling the polarization dependence of SERS intensity as a function of the excitation polarization and polarization direction of the SERS field.

Metal Nanoparticle environment probed using SERS blinking

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We present recent results obtained on the Surface Enhanced Raman Scattering (SERS) properties of Fe₃O₄/Au spherical NPs and triangular Au Nanoprisms.

The hybrid Au-Fe₃O₄ nanoparticles (NPs) were synthesized using a polypol based one-pot method. The nanoparticles consist in quasi-spherical Au cores decorated with magnetite Fe₃O₄ nanoparticles. Optical absorption measurements combined with numerical simulations showed that the Au-Fe₃O₄ nanoparticles exhibit a localized surface plasmon resonance clearly red-shifted with respect to that of bare Au nanoparticles. This plasmonic resonance is exploited to produce surface-enhanced Raman scattering from both the organic molecules and the iron oxide surrounding the Au cores. The SERS signal exhibits strong temporal fluctuations which are used to identify the origin of the observed Raman lines. In particular, we clearly point out the presence of an iron hydroxide (γ -FeOOH) layer at the surface of the Fe₃O₄ nanoparticles forming the shell. Moreover, we investigate the light-induced phase transition from magnetite to hematite (α -Fe₂O₃). Owing to the strong SERS effect we were able to detect the formation of diiron-oxo bonds during the phase transition. These bonds are ascribed to the presence of a mixed magnetite/maghemite phase. The phase transition is triggered by the iron hydroxide surface layer. Such a transition is here studied for the first time in Au-Fe₃O₄ hybrid nanoparticles where the gold cores act as plasmonic nanoheaters responsible for the thermally induced phase transition.

The triangular gold nanoprisms were synthesized following a one pot chemical process and using triethyleneglycol (TREG) and polyvinylpyrrolidone (PVP) as solvent and capping agents. The nanoprisms sustain a strong localized surface plasmon resonance (LSPR) which produces surface-enhanced Raman scattering (SERS) by the PVP and TREG molecules present at the nanoparticle surface. The assignment of the observed Raman features is based on Density Functional Theory (DFT) calculations, performed for various interaction states between the PVP or the TREG molecules and the gold surface. The SERS blinking is analyzed quantitatively using the auto-correlation of spectrally selected temporal SERS traces. We also use SERS covariance maps in order to investigate the cross-correlation between the relevant Raman features. We show that the fluctuations of the PVP and TREG SERS signals are not random. We found that the Raman features associated with the CO stretching vibrations are fingerprints of the interaction between the organic molecules and the nanoparticle surface. The dependence of the SERS blinking on the detuning between the Raman excitation and the surface plasmon resonance is also investigated. We show that the optical excitation plays an important role in the photo-induced chemical processes that occur in the close vicinity of the nanoparticle surface.

Antenna-Enhanced Vibrational Spectroscopy

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Plasmon-polariton excitations of metal nanoparticles can couple to vibrational excitations of similar energies, which enables strong vibrational signal enhancement in the infrared (IR). Due to the highly localized and enhanced near field of a nanostructure, vibrational signals appear up to several orders of magnitudes stronger than the signals in purely vibrational systems. [1]

The talk will explain two different kinds of substrates for surface enhanced IR spectroscopy (SEIRS), which can give an additional enhancement compared to single nanoparticles.

First, additional signal enhancement is achieved by exploiting the extraordinary field enhancement of two antennas interacting across a very small gap in the nm range. Since the preparation of gaps by conventional electron beam lithography is limited in the nm range, we applied photo-chemical induced metal deposition [2] to narrow the gap between two lithographically prepared nanorods. The dimers with shrunken gaps were covered with a 5 nm-thick layer of an organic molecule (CBP) which was used as a near field probe in order to investigate the SEIRS activity in dependence of the gap size. Figure 1 shows a selection of experimental relative transmittance spectra of single nanoantenna dimers with different gap sizes. In the talk we will discuss the additional enhancement of molecular vibrations which can be obtained by using small gaps as a substrate for SEIRS. [3]

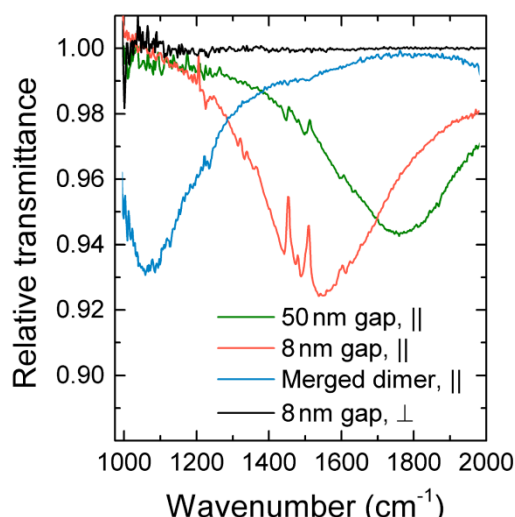


Figure 1: Selection of experimental relative transmittance spectra of individual nanoantenna dimers with different gap sizes, covered with a 5nm CBP layer. [3]

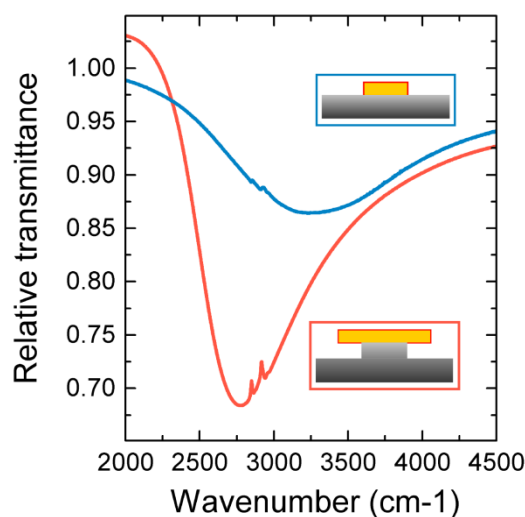


Figure 2: Relative IR transmittance in the spectral region of the fundamental resonance of a planar (blue) and a free-standing (red) gold nanoantenna array covered with one monolayer ODT.

In the second part of the talk we want to introduce nanostructures with reduced substrate effects. Plasmonic nanostructures prepared on substrates with high refractive indices, such as silicon and zinc sulphide, feature lower quality factors, lower extinction cross-sections, and red-shifted resonance positions compared to the low refractive index substrates glass and calcium fluoride. This behavior can be explained by the induced image charges in the substrate, leading to a reduced electron oscillation in the nanorods and thus to lower vibrational signal enhancements in SEIRS. In this contribution we present one way to reduce the undesirable influences of the substrate by fabricating elevated gold nanowires which are only partly in contact with the substrate. We show a comparison of the plasmonic response as well as the SEIRS activity between rods prepared by standard EBL and rods which were additionally treated with reactive ion etching to remove the silicon substrate around the hot-spots of the nanoparticles.

References

- [1] Neubrech, F. et al., *Phys. Rev. Lett.*, Vol. 101, No. 15, 157403, **2008**.
- [2] Härtling, T. et al., *Nanotechnology*, Vol. 21, No. 14, 145309, **2010**.
- [3] Huck, C. et al., *ACS Nano*, doi:10.1021/nn500903v, **2014**.

Plasmonique et spectroscopie : Comment accroître la sensibilité et la résolution spatiale de mesures locales ?

François Lagugné-Labarthe

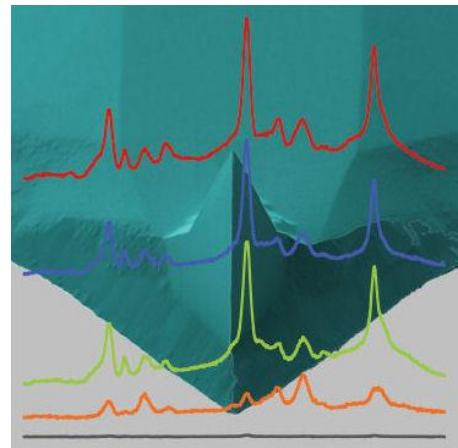
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L'utilisation de nanostructures métalliques est particulièrement intéressante pour des mesures spectroscopiques en Raman ou en fluorescence. Le champ électromagnétique confiné autour d'une particule métallique ou d'un ensemble de particules arrangées périodiquement peut ainsi être mis à profit pour exalter le signal optique émis par des systèmes moléculaires proches de telles structures métalliques. Il en résulte une intensification de plusieurs ordres de grandeur du signal détecté qui varie en fonction des paramètres opto-géométriques de ces nanoantennes métalliques et du milieu dans lequel elles se trouvent.

Dans cet exposé, on développera deux axes qui visent à i) développer des plateformes plasmoniques par lithographie électronique afin de se placer dans les meilleures conditions d'exaltation et ii) à utiliser de tels plasmons de surface localisés afin d'accroître la résolution spatiale ainsi que la spécificité de surface de mesures Raman par effet TERS.

Enfin, nous montrerons comment il est possible de guider des structures biologiques sur de telles structures plasmoniques le but ultime étant de pouvoir détecter en temps réel des échanges biochimiques à l'échelle de quelques cellules. Nous intéresserons en particulier aux réseaux périodiques bidimensionnels de neurones.



RESUMES – ORAUX

Auto-organisations de Nanoparticules d'Argent : application pour la diffusion Raman Exaltée de Surface.

Pierre Aubertin^{1,2}, Lionel Chapus^{1,2}, Alexa Courty², Suzanne Joiret¹, Emmanuel Maisonhaute¹

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La spectroscopie S.E.R.S. exploite l'exaltation du champ électromagnétique au voisinage d'une construction nanométrique appelée "point chaud". Ces points chauds sont créés soit par lithographie électronique soit en dispersant des nanoparticules sur une surface. Une condition importante est d'ajuster la longueur d'onde de la résonance plasmon des nanoparticules à celle du laser utilisé.

Des nanoparticules d'argent de faible distribution en taille (<8%) et pour une large gamme de tailles (2,5 à 7nm) ont été obtenues récemment par réduction de complexes organométalliques $\text{RAg}(\text{PPh}_3)_n$ ($\text{R}=\text{Cl}$, Br or NO_3 and $n=1$ or 3) en présence de thiols [1]. En raison de leur faible distribution de tailles, les nanoparticules s'organisent spontanément sur longue distance en réseau hexagonal à 2D et en réseau cubique à faces centrées à 3D appelé supracristal. Nous avons étudié les propriétés optiques et vibrationnelles de ces organisations en fonction de leur épaisseur.

Nous montrons que les nanoparticules d'argent organisées peuvent être utilisés comme substrat SERS et donnent un fort signal SERS des thiols adsorbés à leur surface. Nous observons également en fonction du nombre de couches de nanoparticules dans les assemblages 3D un ajustement possible de la position de la résonance plasmon à la longueur d'onde du laser utilisé ce qui permet une optimisation du signal Raman et une minimisation des effets parasites telle que la fluorescence. Enfin la nature de l'accroche des thiols sur les nanoparticules d'argent a pu être caractérisée.

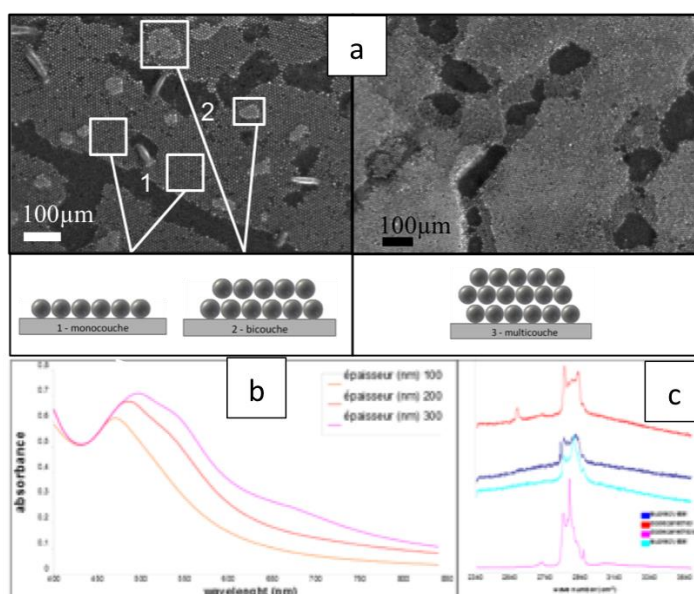


Figure 1 : a) images de microscopie à balayage en haute résolution d'organisations de nanoparticules d'argent, b) Simulation de la réponse optique de supra-cristaux d'argent en fonction de leur hauteur c) spectre SERS d'un supracristal..

[1] A. Andrieux -Ledier, B.Tremblay and A.Courty , J.Phys.Chem.C, 117, 14850-14857, (2013).

Assemblages de nanoparticules en dimères pour la Spectroscopie Raman Exaltée de Surface

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Depuis quelques années, l'assemblage des nanoparticules (NPs) d'or sous forme de dimères est devenu un réel défi dans le contexte des spectroscopies exaltées de surface. Il a été en effet montré que ce type de configuration génère une très forte exaltation locale du champ électromagnétique à l'interstice (de l'ordre du nanomètre) séparant les deux NPs; on parlera de *point chaud*, permettant la détection de molécules à l'état de trace, voire de la molécule unique.¹ Si les techniques lithographiques permettent d'élaborer des nanostructures avec une bonne maîtrise de leur forme et de leur taille, il n'est pas possible de contrôler la distance bord à bord à l'échelle du nanomètre.² Les avancées dans le domaine de la synthèse de nanostructures d'or par voie chimique permettent de s'affranchir de cette dernière limitation. De plus, la distance entre particules et la nature du couplage électronique avec la surface métallique peuvent être modulés à volonté. Cependant, si l'assemblage des nanoparticules en petites chainettes devient maintenant monnaie courante, figer le système à l'état de dimères en solution relève d'un véritable défi.

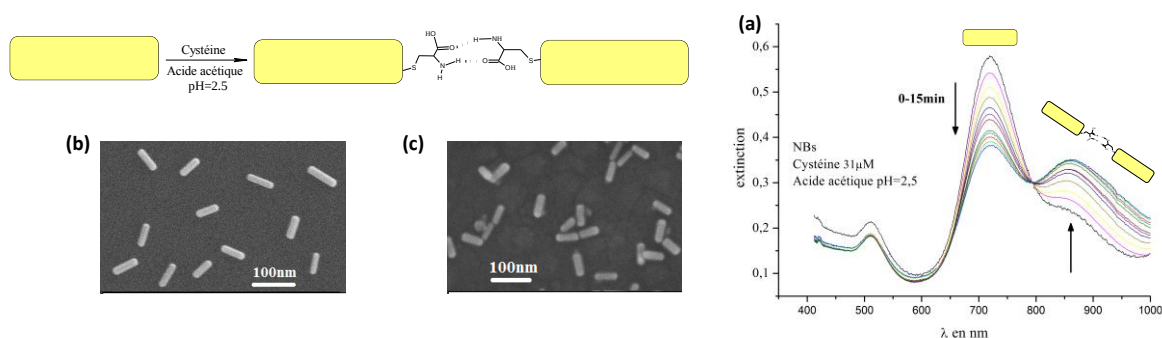


Figure 2: (a) variation au cours du temps du spectre d'extinction des NBs suite à l'ajout de Cystéine 31µM ; (b) Image MEB des NBs avant dimérisation; (c) Image MEB des dimères de NBs.

Dans ces travaux, nous présenterons une stratégie originale d'élaboration de dimères de nanobâtonnets d'or (NBs) en solution. En présence de cystéine, les NBs s'assemblent par liaison hydrogène pour former dans un premier temps des dimères (fig. 1-a).³ Le système est ensuite figé par l'ajout d'ions argent qui tendent à former un chélate avec le reste de la cystéine n'ayant pas réagi. La stabilité de la solution colloïdale obtenue est maintenue pendant plusieurs jours. Le suivi cinétique de la formation des dimères a été mené par spectroscopie UV-visible et spectroscopie Raman exaltée de surface (SERS acronyme en anglais).

Références

- [1] S. Eustis and M. A. El-Sayed, *Chem. Soc. Rev.* **2006**, 35, 209.
- [2] W. Rechberger, A. Hohenau, A. Leitner, *et al.*, *Opt. Commun.* **2003**, 220, 137.
- [3] P. K. Sudeep, S. T. Shibu Joseph, and K. George Thomas, *J. Am. Chem. Soc.* **2005**, 127, 6516.

Exaltation de champ en utilisant de nouveaux modes plasmoniques : couplage entre des plasmons localisés de nanoparticules et les plasmons propagatifs d'un film métallique

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Dans le cas classique d'un film métallique uniforme, la lumière incidente peut exciter les polaritons plasmons propagatifs (PPP) qui sont des ondes évanescentes avec des profondeurs de pénétration typiques d'environ 100 nm se propageant le long de la surface du métal. Les nanoparticules métalliques peuvent confiner les champs électromagnétiques à leur proximité en raison de l'excitation de polaritons plasmons localisés (LPP) par la lumière incidente. Le champ local peut être amélioré dans un réseau périodique de nanoparticules en raison de couplage de la LPP excité dans les particules adjacentes dans la matrice. Ce phénomène est largement utilisé dans un certain nombre d'applications telles que la diffusion Raman exaltée par effet de Surface (SERS), la détection biochimique et de nouveaux dispositifs photoniques. Pour toutes ces applications, il est important d'avoir un fort champ électromagnétique confiné à proximité de la surface du métal

Pour obtenir une exaltation du champ encore plus importante autour des nanoparticules métalliques, nous proposons une nouvelle méthode de couplage entre LPP et PPP, s'appuyant sur la génération de nouveaux modes plasmoniques. Une telle structure est représentée figure 1. Quand la lumière est incidente sur une telle structure, les PPP sont excités et se propagent le long de l'interface métal-diélectrique. La présence du réseau périodique de nanoparticules réfléchit une partie du PPP. Lorsque la condition d'interférence constructive entre les deux PPP est réalisée on observe un champ confiné autour des particules. Ce champ confiné peut exciter les LPP et entraîne une exaltation du champ EM locale autour des particules appelé mode de Bragg (BM). En utilisant un montage de Kretschmann, le couplage entre les PPP et BM, traduit par un mode hybride (HLP) avec le phénomène caractéristique d'anti-croisement. Simulation numériques en utilisant méthode des éléments finis (FEM) montrent que ce couplage augmente l'intensité du champ local autour des nano particules métalliques ce qui améliore le signal pour des applications telles que la SERS et la détection SPR. L'existence de nouveaux modes et l'amélioration de la SERS ont été vérifiées expérimentalement.

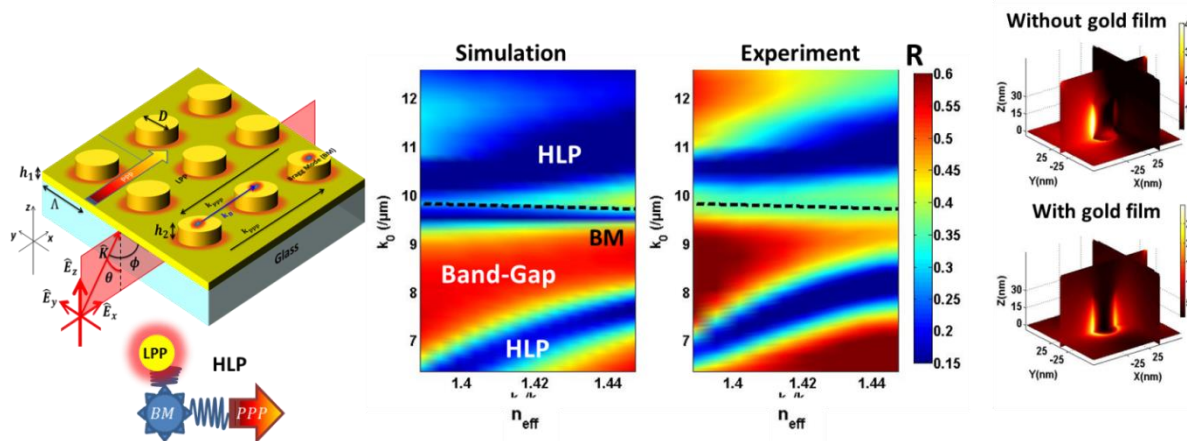


Figure 1 : (à gauche) Biopuce 3D structurée composée de cylindres ($D = 50$ nm) arrangés périodiquement ($P = 200$ nm) sur un film uniforme métallique ($h = 30$ nm) en utilisant la configuration Kretschmann. - (au centre) Nappes de réflectivité angulo-spectrale simulées et expérimentales associées à la biopuce structurée. (à droite) Le champ électrique associé à la biopuce (en haut) pour le mode LPP sans couche uniforme métallique et (en bas) le HLP avec le film uniforme métallique

Points chauds autour d'une nanoparticule

Dominique Barchiesi

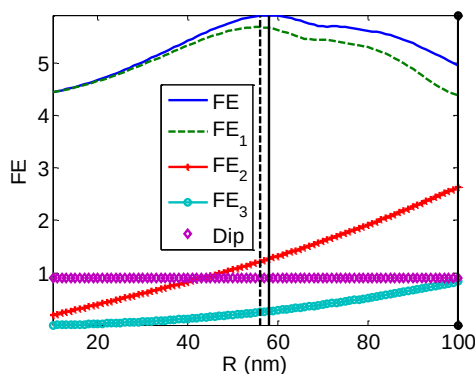
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Les nanoparticules sont utilisées pour augmenter le rapport signal à bruit des signaux de spectroscopie mais aussi de fluorescence. Pour une particule sphérique, la résonance plasmon de surface localisée (LSPR) obtenue pour certaines valeurs de rayon R et à certaines longueurs d'onde d'éclairage a été abondamment observée en champ lointain et peut être calculée en champ proche par la théorie de Mie. Ces calculs connus depuis plus d'un siècle ont donné lieu à des nombreuses publications, calculant la valeur intégrée sur la surface de la particule et plus récemment, des particules de formes plus complexes voire des dimères ont été étudiés à l'aide de la FDTD, de la DDA ou de l'approximation quasi-statique.

Cependant, l'exaltation locale du champ électrique (point chaud) au niveau de la surface d'une nanoparticule sphérique, qui excite les molécules et les fait rayonner requiert le calcul d'une somme de termes (les coefficients de Mie multipliés par les fonctions de base de l'équation de Helmholtz en coordonnées sphériques (harmoniques sphériques) dont on prend le module. Ainsi les divers termes (parfois appelés dipolaires, quadrupolaires...) sont croisés ou interfèrent entre eux. Même pour des particules nanométriques, le dipôle (ordre 0 du développement limité du premier coefficient de Mie autour de $R=0$) n'est en général pas suffisant pour quantifier l'exaltation, notamment car il n'est pas dépendant du rayon des particules, puisqu'il est l'ordre 0 du développement limité au voisinage de $R=0$.

Une analyse de ces termes d'interférence est proposée afin d'expliquer la contribution des coefficients de Mie d'ordre supérieur dans l'exaltation locale du champ (alors qu'elles disparaissent en champ lointain). Pour cela, un développement limité du *champ total* à la surface de la nanoparticule pour de petits rayons de particule, permet de visualiser le couplage entre les différents ordres du développement de Mie et d'évaluer son importance en fonction du rayon de la particule. On montrera comment le point chaud (maximum du champ à la surface de la particule) se déplace par rapport à la direction de polarisation du champ incident, et une étude de la contribution relative de chaque composante du champ total montrera l'évolution de la polarisation au niveau du point chaud, en fonction du rayon de la nanoparticule.

Fig.1 : Exaltation du champ total (FE) en fonction du rayon (R) de la nanoparticule. Contributions des ordres n du développement de Mie (FE_n) montrant l'influence des interférences de l'ordre 1 avec les ordres 2 et 3 pour déplacer la taille optimale de la particule pour un maximum de FE. La particule est en Or (données de Johnson et Christy). Le dipôle (Dip) ne permet pas de rendre compte ni de l'amplitude de FE ni de ses variations.



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Near-field to far-field considerations of SERS measurements on nanocylinders in a periodic arrangement.

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The electromagnetic model of Surface Enhanced Raman Scattering (SERS) is based on near-field enhancement of the electric field. Designing SERS substrate then requires bridging the gap between near-field and far-field properties of nanostructures. This task can be very complex and counter-intuitive [1].

SERS measurement is a way of assessing the near-field enhancement while extinction spectroscopy is a purely far-field measurement. Then combining these two methods enables one to get insight the discrepancy between near-field and far-field optical properties. It was demonstrated that the highest Raman enhancement factor is reached when the excitation wavelength is chosen such as the far-field plasmon band is located at the midway between the excitation and the Raman line wavelengths on nanostructures such as rods [2] or tetrahedrons [3]. Such results tend to prove that there is no significant shift between the near-field and far-field plasmon band positions for these nanostructures. Guillot and co-workers observed that this rule can be applied to small-diameter nanocylinders but not to larger-diameter cylinders [4]. In this case, the optimized excitation wavelength was red-shifted compare to the “midway” rule. Such a work attempts to prove that a red shift becomes significant as the diameter of the nanostructures increases. The aim of this presentation is to investigate this hypothesis by theoretical calculation.

Recently, Zuloaga and co-worker [5] reported a simple approach based on Harmonic Oscillator (HO) model to calculate the near-field to far-field shift from extinction spectroscopy. However, the application of this model failed to explain the discrepancy between the “midway” rule for large diameter cylinders and experimental data. Gold nanocylinders were then modeled by Discrete Dipole Approximation (DDA) using DDSCAT 7.3 [6] to get a deeper insight of the near-field properties (Figure 1). First, we showed that the near-field to far-field shift calculated by the HO model and DDA are very similar. Then we provide an

explanation of the discrepancy from the “midway” rule for large diameter nanocylinders, which does not come from near-field to far-field shift.

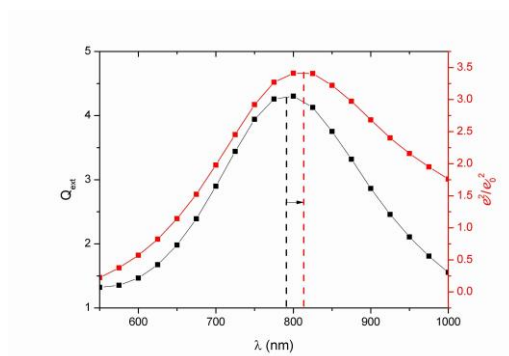


Figure 1 Near-field to far-field shift of an isolated gold nanocylinder of 200-nm-diameter and 50-nm-high. The black curve represents the extinction efficiency while the red one the mean squared electric field density in a 2-nm-thick shell around the nanoparticle.

Acknowledgments

We thank the Remantas project (ANR-11-ECOT-0010) for funding.

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Billion Fold Increase in Tip Enhanced Raman Signal

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Abstract

A billion fold increase in the Raman signal over conventional Tip Enhanced Raman Spectroscopy/Microscopy (TERS) is reported. It is achieved by introducing a stimulating beam confocal with the pump beam into a conventional TERS setup. A stimulated TERS spectrum, closely corresponding to its spontaneous TERS counterpart, is obtained by plotting the signal intensity of the strongest Raman peak of an azobenzene thiol self-assembled monolayer versus the stimulating laser frequency. The stimulated TERS image of azobenzene thiol molecules grafted onto Au<111> clearly shows the surface distribution of the molecules whereas, when compared to the simultaneously recorded surface topography, it presents an image contrast of different nature. The experimentally obtained stimulated gain is estimated at 1.0×10^9 which is close to the theoretically predicted value. In addition to the signal increase, the signal-to-noise ratio was three orders of magnitude higher than in conventional spontaneous TERS. The proposed stimulated TERS technique offers the possibility for a substantially faster imaging of the surface with respect to normal TERS.

ACS Nano, Article ASAP (Web: March 6, 2014).

Un couplage AFM-Raman pour élaborer des nanostructures métalliques exaltantes du spectre Raman, sans contact chimique entre molécules et métal.

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Depuis la découverte de l'effet appelé « Surface Enhanced Raman Spectroscopy » [1] de nombreux travaux pour comprendre et contrôler cet effet ont été entrepris et en faire une liste bibliographique devient aujourd'hui impossible. Ces travaux ont conduit à construire de nouveaux microscopes à sonde locale, microscope TERS pour Tip Enhanced Raman Spectroscopy [2] qui ont supplanté les systèmes à champ proche optique couplé à des spectromètres, à faible capacité d'imagerie [3]. De jolies études sur des nano-objets résonnant ont pu alors être conduites avec cette technique TERS [4] ainsi que sur des monocouches moléculaires [5,6]. Cependant l'effet TERS n'est pas utilisable simplement pour l'ensemble de nos échantillons, en fonction de ses propriétés physiques, nous conduisant à proposer une étude fondamentale couplant la possibilité de manipuler des nanobilles d'argent ou d'or sous un microscope confocal Raman, à excitation laser multi-longueur d'onde. L'objectif est de réaliser des nano-assemblages de nano-particules dans le voisinage de l'objet moléculaire ou du matériaux à étudier, pour profiter suivant la structure de l'assemblage d'un spectre plasmon modulable en longueur d'onde à volonté et de plus éviter un contact chimique avec les structures à étudier.

Nous proposons pour cela une étude consistant en l'élaboration de différentes structures de nanoparticules métalliques (or ou argent) par AFM, couplée à un micro-spectromètre Raman confocale nous permettant d'observer étape par étape l'évolution du spectre de vibration d'un système sonde (typiquement nanotubes de carbone, figure 1a).

Ces données expérimentales s'accompagnent en parallèle de simulations par éléments finis des champs électromagnétiques locaux (figure 1b). Nous arrivons ainsi à une meilleure compréhension d'une part des modes de résonances plasmons de nos nanostructures seules, modes sensibles notamment aux ruptures de leur symétrie, d'autre part aux conséquences de leurs interactions avec un substrat ou une molécule de moment dipolaire connu. Tout ceci nous permettant de mieux comprendre les phénomènes spectraux en longueurs d'onde observés expérimentalement.

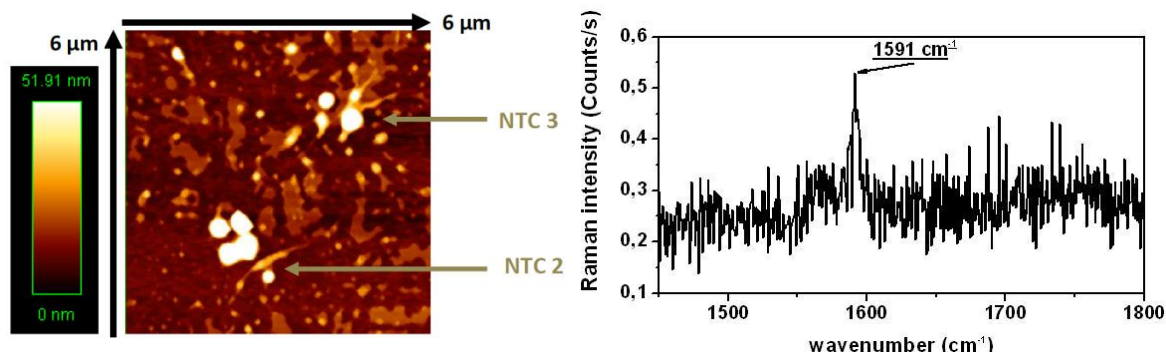


Figure 1a. Exemple à gauche de deux structures générées par manipulation de nanobilles d'or de 20 nm synthétisées par la méthode de Turkévich près de petits fagots de nanotubes de carbone. A droite, exemple d'un spectre Raman uniquement observé avec ce type de structure à 514 nm avec une irradiance inférieure à $5 \mu\text{W par } \mu\text{m}^2$.

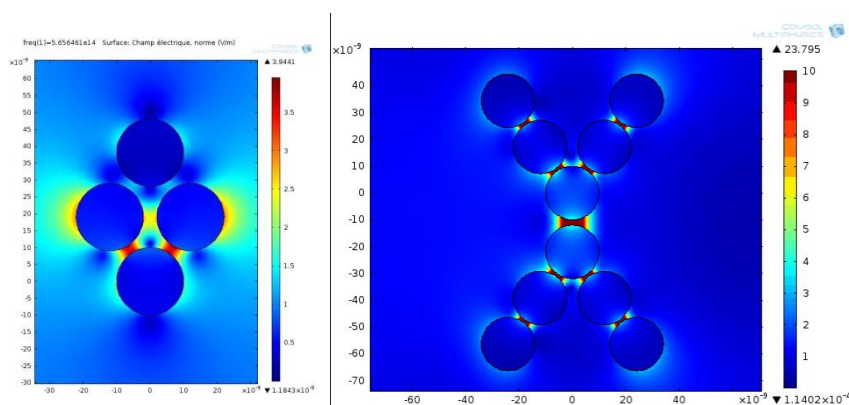


Figure 1b. Simulation en éléments finis d'une nano-structure de nano-particules d'or amplifiant le champ électromagnétique local par effet de pointe et points chauds.

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Lithographic Gold@Polymer Nanorods as Efficient Thermoswitchable Plasmonic Systems for Environmental Sensing Applications

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The patterning of inorganic nanomaterials combined with soft matter can give access to a fascinating class of hybrid structures and properties, in which the stimuli-responsive properties of the soft component can drastically modify the electrical, magnetic, optical or catalytic properties of the inorganic component. If the hybrid system is made of gold or silver nanostructures coated with polymeric shells, their plasmonic properties can be dynamically and reversibly modified or switched provided that an external stimulus or environment (pH, temperature, electrical conductivity...) modifies the physical or chemical properties of the polymer.

In this presentation, we introduce a novel type of lithographic gold nanorods (GNR) coated with a thermosensitive polymer based on poly(N-isopropylacrylamide) (pNIPAM) - GNR@pNIPAM. The atom transfer radical polymerization method was used in order to graft the thermosensitive polymer, and control its thickness. The thickness of polymer brushes grafted on the gold nanorods arrays was directly measured using AFM in water as a function of temperature (from 25 to 42°C). Optical modifications were observed depending on the external temperature, resulting from refractive local index changes due to a phase transition from a hydrophilic state (swollen regime) to a hydrophobic state (collapsed regime) of the polymer chains. Besides their use as a very efficient optical reporter of the polymer state in a controlled and reversible manner (with plasmon shift up to 30 nm), the GNR@pNIPAM structures appear to be of primary importance for applications spanning from opto-mechanical modulators to nanoscale adhesion and environmental sensing.

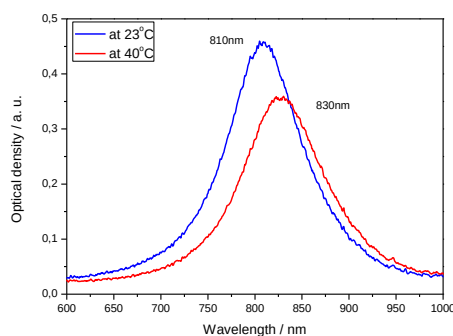
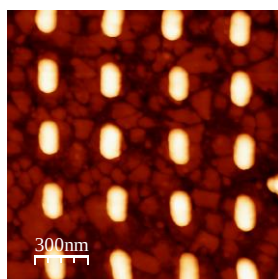


Figure: (left) AFM image of a grating of gold nanorods; (right): corresponding extinction spectra below (23°C) and above (40°C) the temperature of the phase transition of the polymer.

Electrochemically tunable plasmon resonance of gold nanoparticles functionalized by covalently grafted oligomers or by deposited conducting polymers

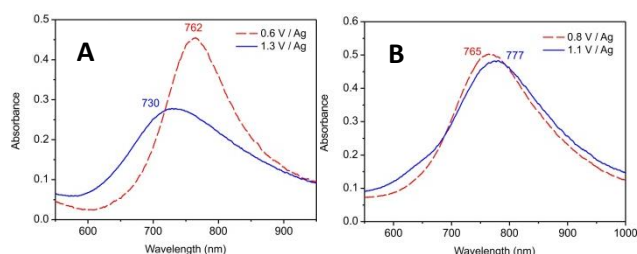
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A large variety of nanometer-scale devices have been investigated in recent years because of the continuously increasing demand for ultimate miniaturization of electronic and photonic systems. Among them, devices based on gold nanoparticles (AuNPs) are well-known for their remarkable properties due to plasmonic effects.

In this context, several active plasmonic devices have been developed. In such systems, an external stimulus can reversibly tune the frequency and/or the amplitude of the plasmon resonance. Several external stimuli have already been employed, based on thermo-, pH-, photo- and redox-responsive layers of molecules surrounding NPs. For instance, we have previously reported electrochemical switching, using redox-sensitive layers based on electroactive conducting polymers such as PANI and PEDOT deposited onto AuNPs gratings (1). Indeed, switches from the reduced non-conducting state and the oxidized conducting state of these conducting polymers lead to a change of the dielectric constant, leading to shifts of plasmon resonance.

In our recent works, we have firstly investigated the influence of the thickness of the surrounding layer of conducting polymer onto the plasmon resonance of AuNPs. We have then compared the effect of deposited conducting polymers with the effect of covalently grafted electroactive oligomers, in order to investigate the influence of the nature of the interaction of the surrounded layer onto AuNPs (2).



Extinction spectra of AuNPs gratings overcoated with deposited polythiophene (A) or covalently grafted bithienylbenzene (BTB, B) in their reduced blocking state and in their oxidized conducting state.

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Phase-sensitive plasmonic metamaterials for biosensing

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Abstract

The presentation will overview latest developments in the frame of bio-plasmonics project focused on the improvement of sensitivity of current state-of-the-art plasmonic biosensors. We extend the original concept of phase-sensitive plasmonic biosensing to new metamaterial-based architectures, which can provide a much improved sensing response, a better cost-efficiency and additional functionalities (e.g., SERS option).

Our on-going project is focused on the improvement of performance of current state-of-the-art plasmonic biosensing technology through the employment of novel metamaterials and sensing principles. Our main approach addresses the employment of phase properties of light instead of amplitude ones in order to improve the performance of plasmonic biosensing technology. As it was confirmed in numerous studies and commercial implementations, such approach makes possible at least 2 orders of magnitude gain in sensor sensitivity in classical thin film geometry of plasmon excitation. We are now extending the phase-sensitive concept to new metamaterial architectures, which are better adapted for modern requirements of bio-nanotechnology and offer new functionalities. Here, we consider several promising nanoscale designs and architectures, including periodically arrayed gold nanodots and plasmonic photonic crystal structures, which support diffractive-coupled plasmon modes yielding to extreme phase singularities. The employment of such singularities promises a breakthrough in sensor sensitivity down to singular molecular level (1 fg/mm² [1]).

Of particular interest we see the implementation of low-cost designs of sensor-oriented metamaterials. We recently employed large-area periodic hexagonal gold nanodot arrays fabricated by fast and low-cost methods of laser-induced forward transfer combined with nanoparticle lithography. We showed that despite relative simplicity of the fabrication technology the structures exhibited extreme phase jumps at points of zero reflection corresponding to the production of diffraction-coupled localized plasmons in the metamaterial array [2]. The recorded sensitivity (10⁵ Deg./RIU) is better than in conventional SPR and is comparable with the one in metamaterial arrays produced by more expensive e-beam lithography methods. Combined with tuneable spectral response and strong local field enhancement, the designed biosensors can outperform conventional plasmonics-based counterparts and open up new opportunities for the advancement of current state-of-the-art biosensing technology.

As another promising activity we consider the employment of nano- and metamaterial-based structures produced by laser ablation in liquid ambience. These nanostructures are exempt of any residual contaminant, which makes them unique for SERS applications. Various geometries based on the combination of optical and SERS/TERS transductions are considered.

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Plasmonic enhanced fluorescence energy transfer

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Förster fluorescence resonance energy transfer (FRET) between donor and acceptor fluorescent molecules is one of the most popular methods to measure distance, structure, association, and dynamics at the single molecule level. However, major challenges are limiting FRET in several fields of physical and analytical sciences: (i) a short distance range below 8 nm, (ii) a concentration range in the nanomolar regime, and (iii) generally weak detected signals.

Plasmonic optical antennas are receiving a large interest to interface light with molecules on dimensions much beyond the optical wavelength. Nanoantennas have been designed for the specific application of enhanced single molecule analysis in solutions at high concentrations, reaching detection volumes down to 58 zL (four orders of magnitude smaller than the diffraction limit) and large enhancement of the single molecule fluorescence, up to 1100-fold [1,2].

Thanks to their ability to control and manipulate optical fields down to the nanometre scale, it is appealing to use plasmonic antennas to enhance the FRET process between single quantum emitters. However, a debate remains open as to determine how the local density of states (LDOS) affects the FRET efficiency and Förster transfer rate [3,4]. In this contribution, we report a thorough analysis of the FRET process into metallic subwavelength apertures. Both donor and acceptor emission channels are investigated simultaneously down to the single molecule regime. This approach enables to quantify independently the LDOS effect on the decay rates and the plasmonic enhancement on the emission. The large fluorescence enhancement and detection volume reduction combine to make nanoantennas a highly parallel platform for studying single molecule dynamics at the biologically relevant micromolar concentration regime [5].

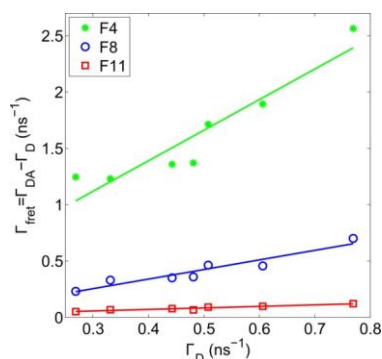


Fig. 1. Dependence of the Förster energy transfer rate on the donor emission rate in the absence of acceptors

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Etude des propriétés de luminescence à 2 photons de nanobâtonnets d'or colloïdaux uniques

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Etant données leurs très fortes propriétés de luminescence de même que leur relative simplicité de fabrication et de mise en oeuvre, les nanoparticules d'or colloïdales continuent de faire l'objet d'un intérêt marqué, notamment en vue d'applications de marquage en biologieⁱ.

Bien que directement corrélée à l'excitation de modes de plasmons localisés, l'origine détaillée de la luminescence de nanobâtonnets d'or reste cependant un sujet controversé. Des études récentes, menées par différents groupes, ont permis de prouver que la luminescence à 1 photon de nanobâtonnets d'or provenait essentiellement d'une relaxation radiative directe du mode de plasmonⁱⁱ. Nous montrons que le cas de la luminescence à 2 photons (2PL) de petits nanobâtonnets d'or (40x10 nm²) semble cependant distinct et implique plus particulièrement la génération puis la recombinaison de paires électrons-trous.

Nous avons mis en oeuvre un banc expérimental associant un AFM à un microscope optique inversé couplé à une excitation par un laser Ti-Saphir ($740\text{ nm} < \lambda < 950\text{ nm}$) de façon à pouvoir faire des études permettant de mesurer simultanément topographie et luminescence à 2 photons de nano-objets uniques. Nous avons pu observer une très forte dépendance du signal de luminescence à 2 photons en fonction de la polarisation laser incidente. La corrélation entre images en topographie et signal de 2PL nous a par ailleurs permis de mettre en évidence un optimum de signal dans le cas d'une excitation du bâtonnet selon son grand axe et à la longueur d'onde correspondant à sa résonance plasmon longitudinale. Enfin, l'analyse spectrale de la luminescence de bâtonnet unique fait clairement état d'une bande d'émission autour de $\lambda=550\text{ nm}$, bien connue pour correspondre à une transition interbande de l'or.

Au-delà de l'étude de l'origine de la luminescence à 2 photons de bâtonnets d'or, nous montrerons enfin que l'analyse approfondie du signal de 2PL peut être utilisé pour une évaluation directe de l'exaltation locale de champ à proximité de la nanoparticule, ce qui est un point clef en vue d'études ultérieures de plasmonique moléculaire.ⁱⁱⁱ

Remerciements :

Ce travail bénéficie d'une aide de l'Agence Nationale de la Recherche portant la référence ANR-12-BS10-016-HAPPLE. Les auteurs tiennent également à remercier le programme C'nano 2010 ainsi que le programme transverse NanoScience du CEA pour leur supports financiers complémentaires.

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La molécule d'aminothiophenol en spectroscopie Raman exaltée de surface

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L'évolution des modes Raman en SERS est souvent considérée comme une signature de l'effet d'amplification d'origine chimique. Parmi les molécules présentant une telle caractéristique se trouve l'aminothiophenol (ou 4 aminobenzenethiol). Cette molécule possède en effet un intérêt particulier pour l'électronique moléculaire, aussi bien pour ses propriétés intrinsèques que la présence des deux fonctions amine et thiol, très utiles en vue de la réalisation d'assemblages moléculaires complexes.

De nombreuses études SERS ont donc été menées sur cette molécule. Ces travaux ont conduit à des conclusions diamétralement opposées. Dans cette présentation je ferai le point sur ces études et montrerai qu'il faut rester très prudent dans l'interprétation de l'évolution des modes Raman en SERS.

Ref :

G. Delafosse, A. Merlen, S. Clair et al.

"A surface enhanced Raman spectroscopy study of aminothiophenol and aminothiophenol-C(60) self-assembled monolayers: Evolution of Raman modes with experimental parameters"

Journal of Chemical Physics, 136, 94704-94704 (2012)

Remerciement : Ce travail a été mené dans le cadre du projet CARIOCA financé par l'ANR.

Nano-plasmonics tuned “click chemistry” monitored *in situ* by Surface Enhanced Raman Spectroscopy

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Surface functionalization and surface chemistry modifications play an important role in many fields, including design of nanosensors. Among all surface modification strategies, “click chemistry” gained meaningful attention for its numerous benefits: high efficiency, simple realization, rapidity, chemoselectivity, feasibility in water media and enhanced yields. UV light-mediated thiol-ene or thiol-yne reactions involve the addition of the thiol to an alkene or alkyne respectively, induced by radicalar mechanism (fig. 1). These reactions have already been reported to allow great diversity of functionalization on several surfaces [1]. Moreover, these reactions also permit multiple functionalization by conjugating other “click chemistry” methodologies.

In approach of multi-targeted molecular sensing in complex environment, design of nanosensor capable to pre-concentrate them selectively is challenging task. For the multifunctional surfaces preparation, several surface-patterning approaches have been proposed, such as photolithography [2], soft lithography [3], electron-beam lithography [4], dip-pen nanolithography [5] and microcontact chemistry [6].

Herein, in order to perform local molecular immobilization at the microscale, thiol-ene click reaction was implemented *in situ* on plasmonic nanostructures using a visible irradiation at 660 nm laser excitation wavelength. The kinetics of reaction was then monitored by Surface Enhanced Raman Spectroscopy (SERS) in real time using the same laser wavelength. We demonstrate the effectiveness of the reaction even if the excitation wavelength is out of the UV range. By investigating reaction rates, on different diameters of nanocylinders made by electron-beam lithography (EBL) (fig. 2), we claim that this reaction is induced by plasmonic effects and by the enhanced electromagnetic field around the nanostructure. In order to prove these assessments various negative controls were performed.

The authors want to acknowledge the ANR REMANTAS project (ANR-11-ECOT-0010) for the financial support.

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TiO₂-Ag⁰ plasmonic sensor for the SERS detection of organic molecules

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The detection of different biomolecule analytes from the food industry, pharmaceuticals or human body such as proteins, drugs, glucose, DNA and nucleotides by plasmonic sensors is nowadays an extensive subject of research. Notably, the Surface Enhanced Raman Spectroscopy (SERS) technique provides a powerful, rapid, and sensitive way to analyze the structural fingerprint of molecules through the detection of their specific Raman peaks. In this aim, versatile methods are proposed to generate highly efficient SERS substrates. The latter are mainly Ag⁰ nanoparticles (NPs) colloidal suspensions [1] and in a lesser extent solid SERS active substrates such as roughened electrode [2] or Ag⁰ NPs bounded on Si surface [3,4]. To get efficient and reproducible SERS signal, several key points are still challenging. On the one hand, the substrate must provide “hot spots”. It requires the control of the size, shape and distance between the Ag NPs as well as their good adhesion on the solid surface. On the other hand, the efficient adsorption as well as the correct orientation of the analyte molecules on the Ag⁰ NPs is extremely important.

We report the promising, new and low cost SERS substrates composed of Ag⁰ NPs distributed over a TiO₂ film (Fig. 1). The whole substrate elaboration involves simple wet chemistry routes. It benefits from the specific photo-induced properties of TiO₂. The deposition of Ag⁰ NPs has been performed through a photocatalytic reduction process on the surface of sol-gel deposited TiO₂ thin film. Notably a tri-sodium citrate (TSC)-assisted photocatalytic reduction process and an ascorbic acid (AA)-based seeded growth procedure has been developed to monitor the growth of Ag⁰ NPs on the TiO₂ surface. As a result, the NP size is ranging between 50 and 100 nm with a covering rate of 50% (Fig. 2).

Firstly, the performances of such Ag⁰/TiO₂ SERS substrates have been validated using Rhodamine 6G as a model molecule. It features good SERS performances: a 10⁶ enhancement factor and a detection limit close to 10⁻⁹ M, as well as a good reproducibility of SERS spectra (13 % standard deviation on 16 spectra) on large dimension substrates (over an area close to mm² scale) [5].

Secondly, the label-free SERS detection of single strand DNA monobase sequences (poly-adenine, poly-guanine, poly-thymine, and poly-cytosine) as well as multibase sequences has been performed with minimal additional sample preparation. We thoroughly investigated the signals by varying the DNA concentration from 10⁻⁴ to 10⁻⁶ M. In the case of monobase sequences, highly resolved spectra have been obtained even for section poly-C and poly-T which have low Raman cross-section (Fig.3-4). For all sequences, the intensities of the main base peaks showed clear concentration dependence. An optimum of concentration is found between 5 and 10 μM which can be correlated with some re-orientations of DNA molecules with respect to the Ag NP surface [1,3].

Our results on DNA detection will be presented. They allow us to expect that this new and low cost Ag⁰/TiO₂ SERS substrate will enable to process new label-free and target-specific sensors for sensitive in-situ monitoring applications.

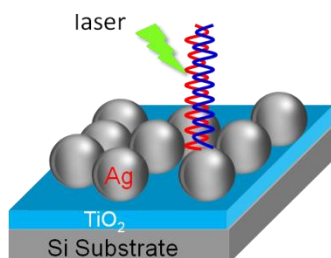


Figure 1. label-free DNA detection scheme

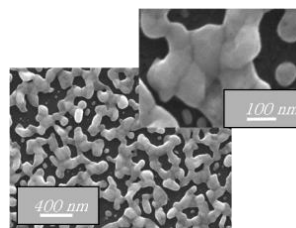


Figure 2. FEG-SEM images of Ag° NPs formed through a seeded growth TSC (trisodium citrate)-assisted photocatalytic process in top-view.

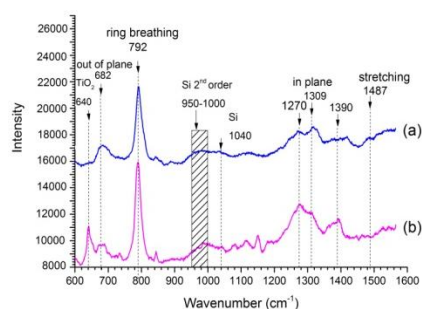


Figure 3. SERS spectra of poly-cytosine collected on Ag°/TiO₂ substrate. Measurements were performed for concentration: 10 μM (a), 5 μM (b).

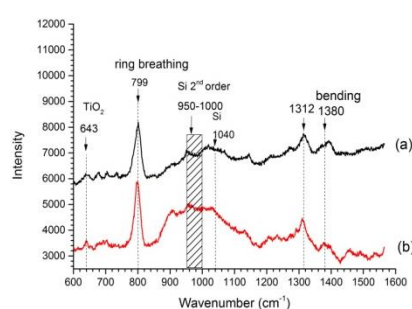


Figure 4. SERS spectra of poly-thymine collected on Ag°/TiO₂ substrate. Measurements were performed for concentration: 10 μM (a), 5 μM (b).

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RESUMES – POSTERS

FUNCTIONALIZATION OF GOLD NANORODS BY MOLECULARLY IMPRINTED POLYMERS FOR EXTRACTION, DETECTION OR DRUG RELEASE

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Anisotropic gold nanorods (GNRs) have received a great deal of attention recently due to their large absorption cross-section in near-infrared frequencies which opens new opportunities for localized hyperthermia in cancer therapeutics^[1]. Their use generally requires their functionalization in order to protect colloidal particles from aggregation, to manipulate the optical, electronic and catalytic properties of the gold core, as well as to control interfacial properties. At the same time, **molecular imprinting** has become a widely used method for creating ligand-specific polymeric materials with recognition properties analogous to biomolecular systems^[2]. Combining the exceptional characteristics of molecularly imprinted polymers and anisotropic gold nanorods in a single system should afford a hierarchical structure enabling the hybrid particles to report quickly, easily, sensitively and directly a molecular recognition event **without any transducers and treatments** for analytes (label-free). In this poster, I will present an original method for the functionalization of gold nanorods by molecularly imprinted polymer layers. The recognition properties of these new hybrid systems will also be investigated.

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Étude des transferts d'énergie dans des particules cœur-coquille individuelles

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Nous présentons les résultats obtenus dans l'analyse des propriétés optiques de nanoparticules hybrides de type cœur-coquille. Il s'agit de nanoparticules de 50nm de diamètre composées d'une coquille de silice contenant des molécules d'isothiocyanate de fluorescéine (FITC) entourant un cœur d'or de 5 nm. L'objectif de nos expériences est d'identifier les mécanismes de transfert d'énergie possibles entre le cœur en or et les molécules excitées qui servent de réservoir d'énergie. Les résultats sont déduits de l'étude comparative de l'émission de ces particules et de l'émission de particules de référence i) avec un cœur en or et une coquille sans molécules FITC et ii) de particules uniquement en silice contenant des molécules de FITC. Les particules sont dispersées dans l'eau.

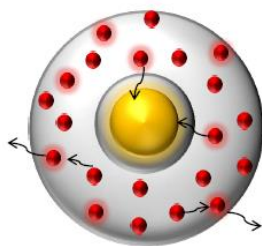


Fig. 1 : Nanoparticule hybride de type cœur-coquille.

Lors de nos expériences, nous avons utilisé deux méthodes complémentaires de spectroscopie à l'échelle de la particule unique. La première est la spectroscopie de corrélation de fluorescence (FCS). Elle est fondée sur l'analyse des fluctuations temporelles de l'intensité de la fluorescence. Elle fournit le temps de diffusion des particules ainsi que leur durée de vie. Cette méthode a permis de mettre en évidence une réduction de la durée de vie de l'émission de fluorescence des nanoparticules cœur-coquille dopée lorsque la puissance d'excitation augmente.

La seconde technique est une méthode de spectroscopie de temps de vol (TOFPS), qui permet d'acquérir le spectre d'émission des nanoparticules qui diffusent une par une dans le volume d'excitation du microscope confocal. Elle a permis, dans certaines conditions, de mettre en évidence l'apparition d'une raie supplémentaire dans le spectre d'émission de la nanoparticule, dont la longueur d'onde est proche de celle de la résonance plasmon de la particule en or.

La combinaison du rétrécissement de la durée de vie de l'émission avec la modification de son spectre d'émission peuvent s'expliquer par l'existence d'un transfert d'énergie du milieu moléculaire vers la particule qui se désexcite alors radiativement. Ce type de transfert est à l'origine de l'effet SPASER¹ précédemment observé (Surface Plasmon Amplification by Stimulated Emission of Radiation)

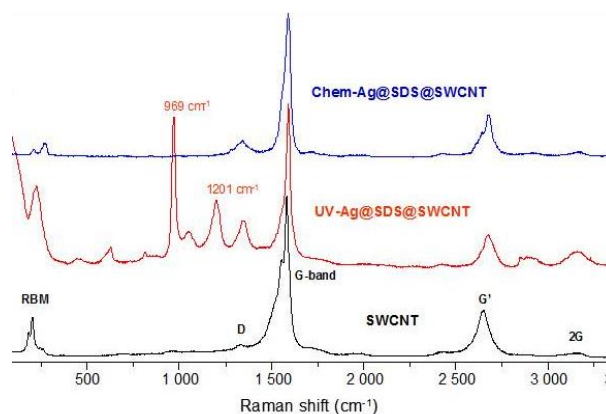
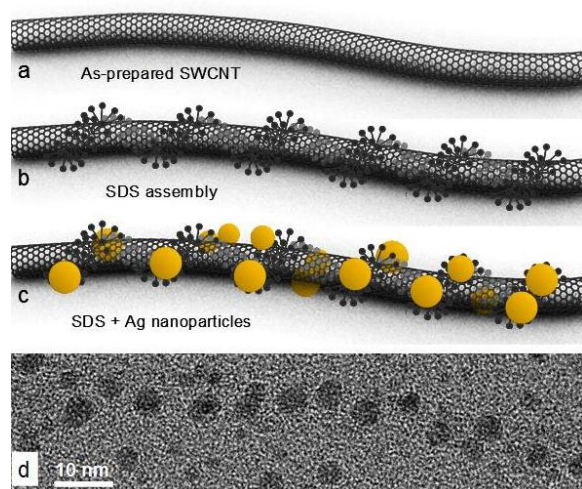
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Raman scattering of linear chains of strongly coupled Ag nanoparticles on SWCNT

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We compare the Raman scattering properties of hybrid nanostructures consisting of Ag nanoparticles (NPs) in disordered and aligned arrangements on single-walled carbon nanotubes (SWCNTs) as a result of chemical and photoreduction methods. In the latter case, the unique structure of the very small Ag NP (from 4 to 7 nm) chains generated an extremely large mode at 969 cm^{-1} that was assigned to the sulphate-silver interaction at the NP surface. Another strong mode was present at 1201 cm^{-1} and was assigned to an IR-active mode of SDS; this mode was observed because the symmetry changes altered the selection rules. We demonstrate that both the UV photoreduction of silver and the presence of SWCNTs are necessary to produce this very strong Raman scattering. The Raman modes of the SWCNTs are also significantly modified by the presence of Ag NP chains along the nanotubes.

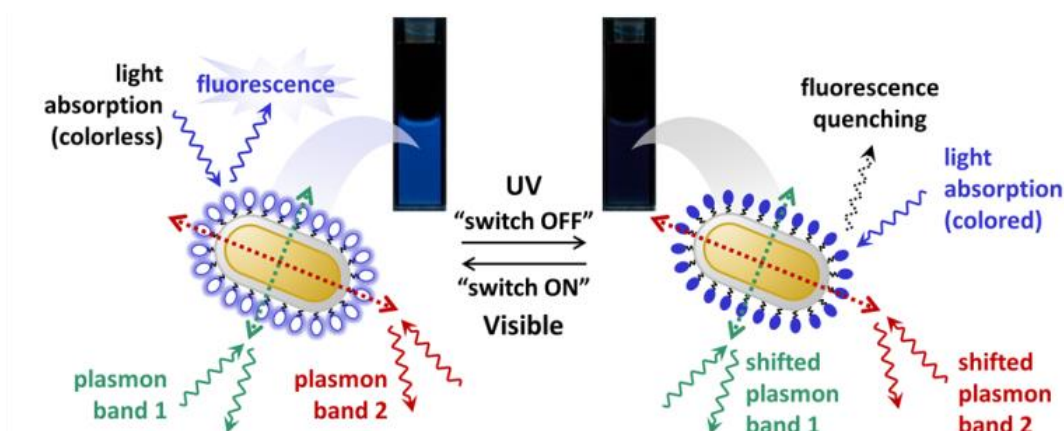


Three-component hybrid systems photochromic / fluorescent / plasmonic nanomaterials for enhanced photoactivity

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Hybrid nanomaterials combining gold nanoparticles and photochromic compounds show growing interest due to the wide field of applications especially as optical switches for data storage. As the coupling mechanism is not precisely known, we deposited photochromic molecules on gold nanospheres and irradiated this hybrid film under UV and visible light. Clear modifications of the plasmon band are observed under these conditions showing coupling between the two units. Considering this coupling and the one between fluorescent molecules and metallic nanoparticles, we designed, synthesized and characterized a multi-component hybrid nanosystem composed of a plasmonic gold nanorod core functionalized by molecules displaying both photochromic and fluorescence properties. Accurate control of the distance between the plasmonic core and the photoactive organic counterparts has been achieved by means of a silica shell. Spectroscopic investigations demonstrated that cross-coupled interactions between plasmonic, photochromic, and fluorescence properties play a major role in such nanosystems, depending on the thickness of the silica spacer. Although these two effects have already been studied separately, this is the first attempt to build a three-component hybrid system showing both couplings in the same composite nanostructure. Moreover the fluorescence signal is tightly related to the photochromic state of the molecules, ensuring complete cross-talks between the three properties.

We built an hybrid system where up to five output signals can be exploited and switched by light : (i) light absorption of the colorless state of the photochromic molecules, (ii) light absorption of the colored state, (iii) fluorescence emission of the molecules, (iv) light scattering of the traversal and (v) longitudinal SPR of the GNR. We believe that such “colored-fluorescent-plasmonic nanophotoswitches” are extremely promising in the field of smart and integrated photo-controllable nanodevices, and we are currently investigating their detailed optical properties down to the single particle level by means of appropriate microscopy and spectroscopy methods.



Study of gold-molecule interaction based on SERS spectral fluctuations analysis

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In this contribution, we report the interest of the Surface Enhanced Raman Spectroscopy (SERS) spectral identification based on Principal Component Analysis (PCA) [1].

To that purpose, we design an active SERS template based on surfactant-less Chebyshev nanoparticles operating in a microfluidic platform and mounted on a high numerical aperture confocal microscope [2].

The PCA of the fluctuating spectra sorts the reference spectra of the molecule of interest [3] (Fig.1). The assignment of the Raman bands brings new insight into the orientation of the molecule in interaction with the gold surface, according with the theoretical point of view developed by Pr Moskovits thirty years ago [4] (Fig.2).

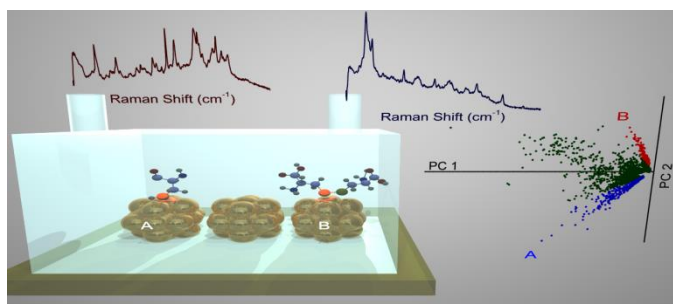


Figure 3: Coupling of a microfluidic platform with surfactant-less Chebyshev nanoparticles to apply Principal Component Analysis

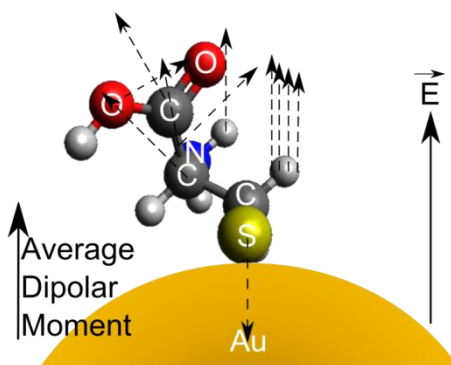


Figure 4: Cystein-gold complex orientation based on SERS spectrum analysis

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Instrumental coupling of SPRI and SERS for multi-modal biosensors

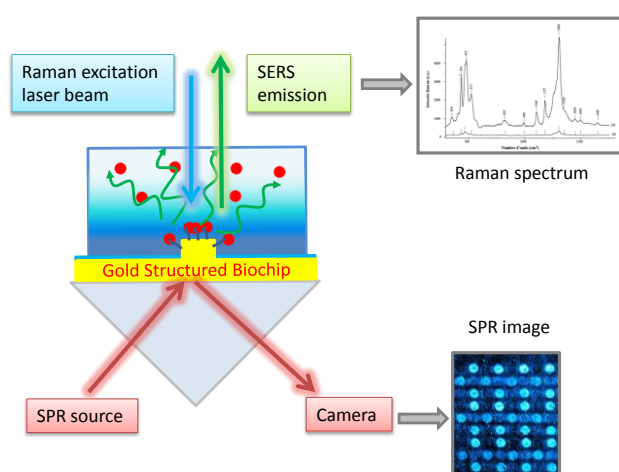
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surface plasmon resonance (SPR) sensing is a well-established technique in the biomedical field, where real-time and label-free detection is particularly useful to monitor the binding of target biomolecules onto a flat gold biochip. Conventionally, the grafting of probe molecules that recognize specifically the molecules of interest is realized thanks to a surface chemistry protocol on the gold surface. As a result, the selectivity of the measurement strongly depends on the surface chemistry quality and the probe-target interaction specificity. Furthermore, standard SPR sensors have reached their limits when considering the noise of the light source and detector intrinsic to the instrumental system. Both concerns restrain the limit of detection of a SPR biosensor to a concentration of target molecules around 1nM, which is not sufficient to analyze trace molecules such as food contaminants or cancerous markers.



This statement motivated the following study which consists in improving the sensitivity and specificity of plasmonic biosensors. First, the robustness of the SPR technique is improved by the use of a multispectral interrogation based on five wavelengths. Then, it is possible to analyze in parallel and real time a great number of biomolecular interactions. Moreover, by coupling Surface Plasmon Resonance Imaging (SPRI) and Surface Enhanced Raman Scattering (SERS), the measurement is rendered more accurate and specific thanks to the additional data of the fingerprint of the captured molecules provided by the Raman spectrum. This ANR project, named Piranex, which involves a large consortium of laboratories, will lead to the design of a unique bimodal instrument capable of detecting trace molecules.

Fig 1 – Multi-modal instrumentation coupling SPR and SERS measurements

Furthermore, to amplify the detection signal, the gold biochip is nanostructured to enhance both SPR and Raman signals. Nanoparticles confine the electromagnetic field at their vicinity, making the detection less sensitive to changes occurring in the dielectric surrounding medium (Fig.2) and enhancing the molecular vibrations of the targeted biomolecules. Therefore, the SPR signal is rendered more robust towards environmental perturbations and the SERS emission is more efficient.

Thus, coupling of SPR imaging and SERS will allow going beyond the resolution limit of conventional SPR sensors with an improvement of the sensitivity and specificity of the detection.

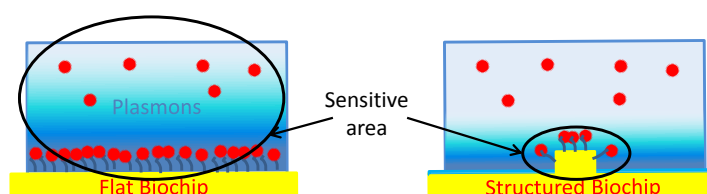


Fig 2 - Confinement of the field by gold nanostructures

Enhanced fluorescence emission from resonant DNA assembled plasmonic nanoantennas loaded with single dye molecules

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Because of homogeneous broadening effects, single organic molecules exhibit weak absorption cross-sections at room temperature even though they feature large dipolar transition moments for their electronic excited states. We recently demonstrated, by a conjunction of time-resolved luminescence and fluorescence correlation spectroscopy, that gold nanoparticle (AuNP) dimers can be used to enhance reproducibly the excitation cross-sections and decay rates of organic dyes by more than one order of magnitude [1]. We use 40 nm diameter AuNPs linked by a single DNA strand as short as 10 nm and electrophoretic purification to obtain a stable suspension of dimers [2]. By controlling the number of DNA linkers, we ensure that only one quantum emitter is attached per nanostructure, allowing single photon emission with reduced lifetimes [3]. These nanostructures behave as the optical equivalent of a dipolar antenna driven by a single photon source. In order to optimize the quantum yield and excitation probability of these emitters, we increase the size of the AuNPs and the scattering cross-sections of the antenna in order to reach an average 44 times enhancement of the fluorescence count rate with picosecond lifetimes. These values correspond to unprecedented dipolar transition moments of isolated quantum emitters at room temperature, and investigate the coupling of single quantum emitters to resonant dipolar antennas. We achieve 200x lifetime reduction while preserving bright emission of single photons.

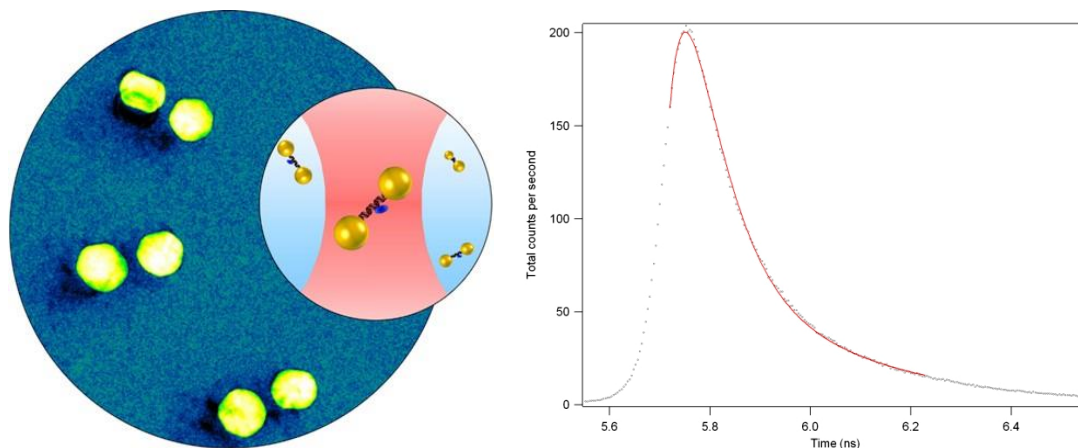


Fig. 1. Cryo-EM image of DNA-templated 40 nm AuNP dimers with 17nm gap. A single fluorescent Atto647N molecule is inserted in the DNA linker to act as source element for the plasmonic antenna, realizing bright emission with picosecond lifetime.

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Nanoantennas for enhanced single molecule detection at high concentrations

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Plasmonic Nanoantennas are promising tools to control and manipulate optical fields at the nanometer scale [1]. We study nanoantennas using both top-down (FIB milling) and bottom-up (colloidal synthesis) approaches. Here, we present the effects of two nanoantennas, Antenna-in-box (FIB) [2] and Gold Nanosphere (colloidal synthesis) [3] to enhance single molecule detection at high concentrations, **Fig.1**.

In both cases, Fluorescence Correlation Spectroscopy measurements are done to detect the Fluorescence of Alexa Fluor 647 molecules at micromolar concentrations in a solution containing 200 mM of Methyl Viologen (MV). This concentration of MV quenches the quantum yield of Alexa 647 from 30% to 8%. Fluorescent emitter of low Q.Y. can sense higher fluorescence enhancement factors than Higher Q.Y. emitters.

Antenna-in-box design combines fluorescent signal enhancement and background screening, offering high single-molecule sensitivity (fluorescence enhancement up to 1,100-fold and microsecond transit times) at micromolar sample concentrations and zeptolitre-range detection volumes. With the large fluorescence enhancement and detection volume reduction, this device can be optimized for single-molecule fluorescence studies at physiologically relevant concentrations. Colloidal nanoparticles represent an inexpensive and versatile platform to enhance the fluorescence detection at the biologically relevant micromolar concentration regime. We demonstrate detection volumes down to 270 zeptoliters (three orders of magnitude beyond the diffraction barrier) together with 60-fold enhancement of the fluorescence brightness per molecule.

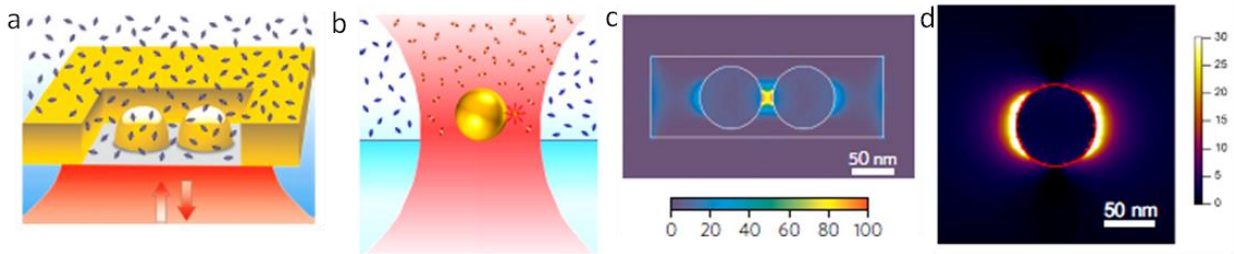


Fig. 1: a) and b) Schematic of Antenna-in-box design and Gold Nanoparticle on a glass substrate, respectively c) and d) FDTD computation of excitation intensity enhancement for Antenna-in-box design and 80 nm gold nanoparticle, respectively.

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Nanostructuration de film d'or sur verre pour la biodétection : Exaltation de phénomènes physiques tels que le signal Raman et les Plasmons de Surface.

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Les biocapteurs sont utilisés dans de nombreux domaines afin de répondre aux nouvelles normes sanitaires et environnementales ainsi qu'aux besoins dans le monde de la médecine ou le domaine de la sécurité.

Dans cette optique, la fabrication d'échantillons est une étape incontournable afin de développer et d'améliorer les biopuces actuelles. La nano-structuration de la surface est une des voies envisagées par la communauté scientifique actuelle afin d'exalter certains phénomènes physiques utilisés en biodétection comme les plasmons de surfaces ou l'exaltation Raman. Les motifs, les périodicités et les dimensions des nanostructures sont autant de paramètres à prendre en compte afin d'améliorer la sensibilité des biocapteurs. Tous ces paramètres demandent un savoir-faire expérimental d'autant plus lorsque la nature du substrat est différente du silicium. Nous travaillons sur des substrats de verre recouverts d'une fine couche d'or. Les nanostructures, ici des nanodisques et des pistes, sont réalisées par deux voies : la lithographie électronique (EBL) et la nano-impression assistée par UV (UV-NIL). Les dimensions obtenues dépendent de la technique de fabrication mais les diamètres/largeurs sont compris entre 60 et 200 nm avec des périodes de 120 à 500 nm. Les structures obtenues sont ensuite caractérisées expérimentalement par mesure de diffusion Raman exaltée par effet de Surface (SERS). Elles sont également caractérisées sur un banc d'imagerie permettant l'interrogation angulo-spectrale de la réponse plasmonique de la biopuce. Ces deux caractérisations permettent de montrer le réel impact des nanostructures sur la biodétection.

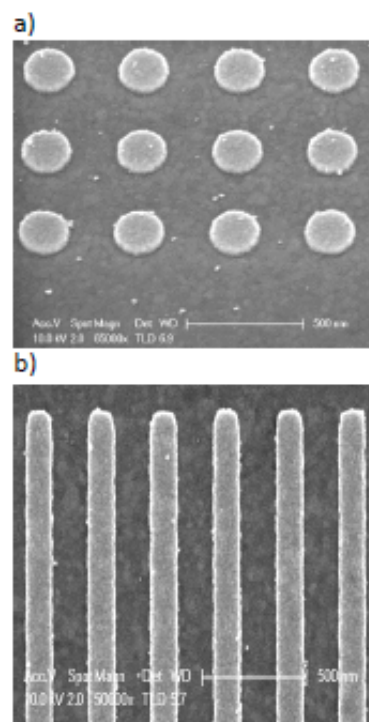


Figure 1: Images MEB pour des nanodisques (a) ($d=200$ - $p=400$ nm) et des pistes (b) ($l=100$ - $p=300$ nm).

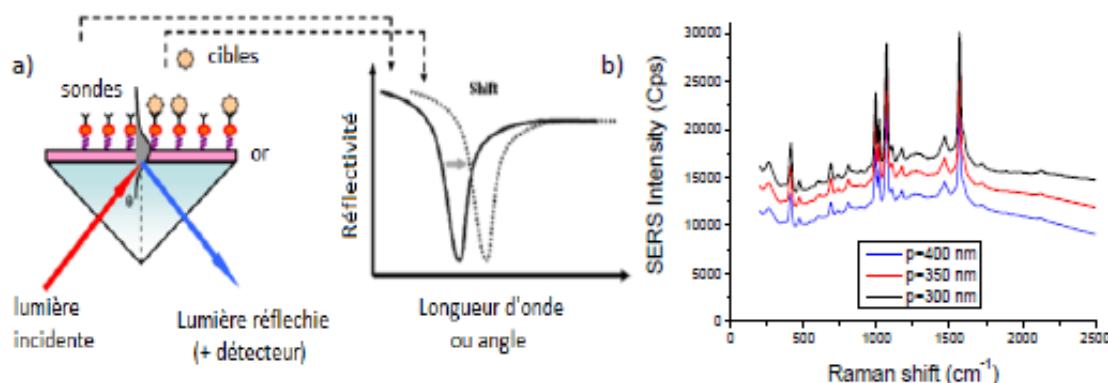


Figure 2 : Schéma de principe de la réponse d'un biocapteur SPR (a) et Mesures expérimentales SERS montrant le rôle de la période (b).

Gold Nanoparticles for Plasmonics

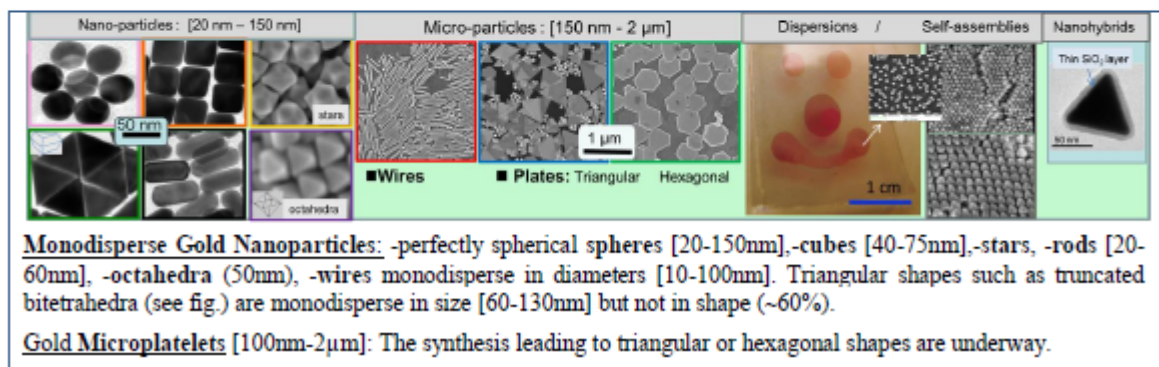
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Our research concentrates on the synthesis and self-assembly of gold nanoparticles and nanohybrids for plasmonics that is a rapidly growing discipline at the interface of physics, chemistry and biology due to promising applications in key areas such as energy and health. Noble metal nanoparticles have the ability to confine very high electromagnetic-field intensities at their surface. In hybrid "metal/chromophore" nanostructures, this antenna effect is used to enhance linear and nonlinear phenomena.

We use colloidal chemistry to synthesize gold nano- and micro-particles of controlled shape and size. This control of the morphology provides a fine tuning of the plasmon resonance wavelength and of the local field enhancement factor. Compared to top-down materials, these gold particles of high crystalline quality offer better surface-confinement of the electromagnetic field. We uniformly disperse these particles on substrates at various densities over large areas. We investigate their spontaneous self-organization leading to the formation of 3D arrays. Silica-coated gold nanohybrids are synthesized with a thin silica layer for tuning their antenna properties.

The performances of the various nanodevices made from these particles are studied in collaboration with academic research laboratories expert in the different fields of plasmonics (see ref. below).



Acknowledgements: this work is financially supported by ANR (Happle project) and the Région Ile-de-France (DIM Nano-K, Cossmet project).

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