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# Planar Au meta-surfaces as broadband radial polarizers

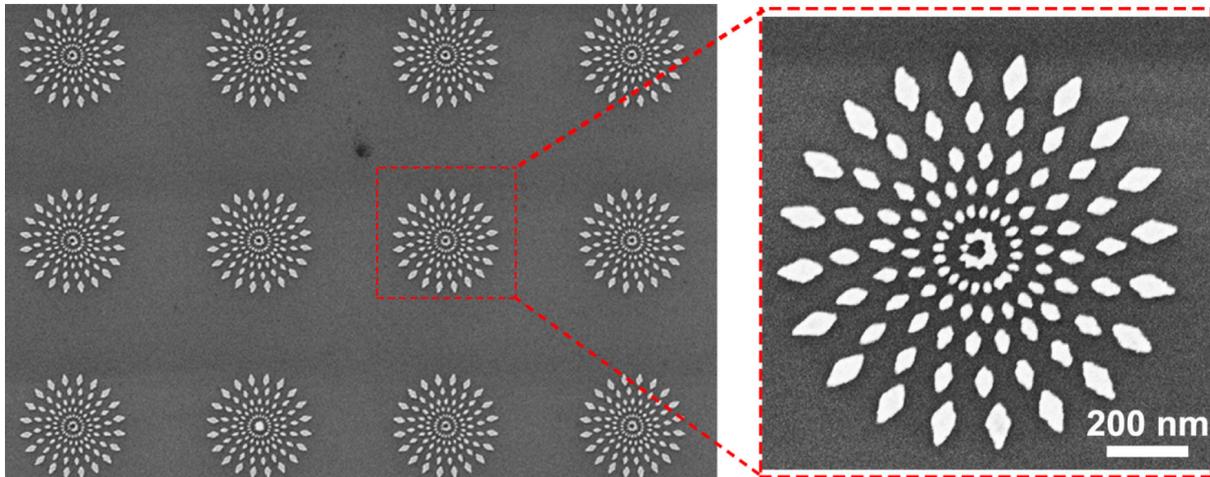
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Planar meta-surfaces consisting of gold nanostructures with specifically designed geometries are a promising approach for novel optical components that opened the field of flat optics.<sup>1,2</sup> The moulding of the phase of the light on the nanoscale can, for example, result in lensing effects without the requirement of an extended optical path length for the modulation. Another exiting direction is the modulation of the polarisation and of the spatial distribution of the light intensity to obtain functional optical components.<sup>3</sup>

In our study, we chose a rhombus shape as the basic component for the meta-surface structures and use a mathematical algorithm to compute their arrangement for obtaining the desired functionality. We demonstrate this approach by fabricating near-field broadband radial polarizers as depicted in Figure 1. The optical properties of such flower-like meta-surfaces are studied by Fourier-Transform infrared absorption, finite element method simulations, and two-photon hyperspectral imaging.



*Figure 1. Scanning electron microscopy images of an array gold nanostructures fabricated by electron beam lithography that function as broad band radial polarizers*

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# Reversal of anisotropic optical properties of a gold nanoparticle/smectic liquid crystal composite film through heating

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Gold nanoparticles are studied a lot in relation with their plasmonic properties. It is well known that when gold nanoparticles are close enough, the electromagnetic coupling modifies the plasmonic properties. This is the reason why more and more research focuses on controlling the self-assembly of nanoparticles. Liquid crystals are very good candidates for this purpose since they usually contain disordered areas called topological defects which can be used for nanoparticle trapping. In this work we embedded gold nanoparticles in a smectic liquid crystal structure (Figure 1) made of arrays of parallel dislocation lines (linear defects)<sup>1</sup>.

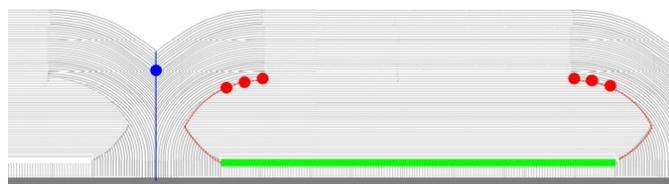


Figure 1. Full model of the structure of oily streaks, presented in side-view in the plane perpendicular to the hemicylinders axis. Blue line : curvature wall, red dotted lines : rotating grain boundaries, green area : central defect, red and blue dots : dislocations lines parallel to the hemicylinders axis

Measurements of the plasmon resonance of the gold nanospheres indicate that we can obtain nanosphere chains parallel to the direction of the dislocation lines over large scales, in agreement with a trapping phenomenon of the nanoparticles by the dislocations<sup>2, 3</sup>. We here demonstrate a drastic change of the organization of the nanoparticles when the composite material is heated towards another liquid crystal phase called nematic. We evidence a rotation of the nanoparticle chains that become perpendicular to the direction of the oily streaks. This phenomenon is interpreted by a de-confinement of the nanoparticle when the topological defects disappear in the nematic phase, the nanoparticle becoming free to reorganize in the nematic phase. The perpendicular chains appear to remain stable under cooling back in the smectic phase in relation with the presence of the central grain boundary as an alternative trapping area (in green on Figure 1). Finally, these results show that we are capable of anisotropy switching of the gold nanoparticles extinction through the evolution of the liquid crystal matrix with temperature.

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# Cross-talking interaction in plasmonic/photochromic nanomaterials

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Molecular photoswitches have attracted considerable interest in the last few decades in the field of molecular electronics and photonic devices. Among the different possible molecular photoswitches, photochromic molecules show many advantages based on the reversible modification of their chemical structure under light irradiation. Many photochromic compounds have been studied but the diarylethene (DAE) molecules are particularly interesting since they present a great bistability and a high fatigue resistance.<sup>1</sup> Using photochromic molecules to modulate other photophysical properties such as fluorescence is very promising for applications because it offers time and space control. Thus the idea of coupling a photochromic unit with a plasmonic unit is very interesting and for example Feringa and co-workers<sup>2</sup> showed that such hybrid materials could be used to induce a switch of the molecular conductance by light excitation. But such a coupling between these two units is still improperly known. Several consequences have been demonstrated: it can lead to a shift or modification of the surface plasmon resonance under light irradiation<sup>3</sup>, a decrease of the photochromic activity<sup>4</sup>, an irreversibility of the photochromic reaction<sup>2</sup> or an improvement of the photoswitching efficiency<sup>5</sup>. These backward issues are explained by the crossed influence of the photochromic unit with the plasmonic unit.

Here we present synthesis and experimental results of hybrid systems showing coupling between plasmonic and photochromic units. We will see how the photochromism can modulate the plasmonic properties and how the gold unit can influence the photochromic reaction. Controlling such cross-talking interactions is complex and many key parameters have to be taken into account. By using different shaped nanoparticles (spheres, rods) and different functionalization (silica shell, polyelectrolytes), we will identify these key parameters and see how we can optimize the cross-talking interaction between the photochromic and the plasmonic units. Such experiments have been done using absorption (Figure 1), continuous photolysis and SERS spectroscopy.

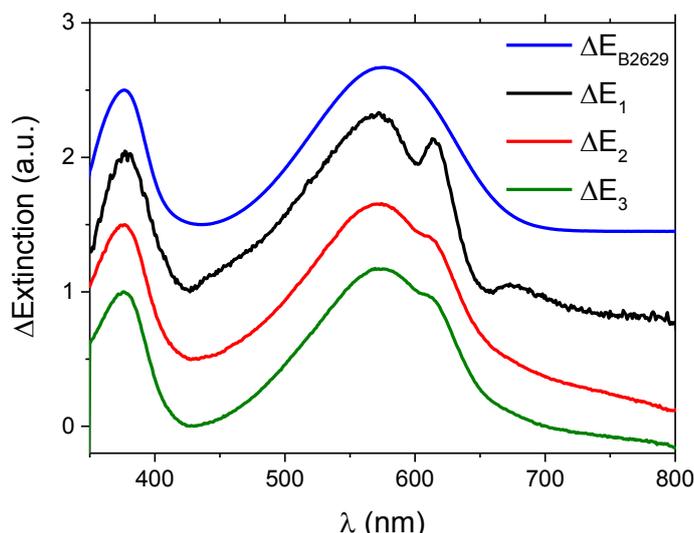


Figure 1. Differential extinction spectra calculated by subtracting extinction spectra measured before from the one measured after the photochromic reaction. Blue curve is the DAE molecule without gold nanorods, black, red and green curves are the DAE molecule with gold nanorods of different aspect ratio. Spectra have been vertically shifted for clarity.

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# RB@Au/mSiO<sub>2</sub> core-shell nanobipyramids for the enhanced-production of singlet oxygen

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Gold nanomaterials display interesting nanoplasmonic features with potential application in various fields depending on the size and shape of the metal nanoparticle. The size and geometry of Au NPs can be tuned by simply changing the experimental parameters in order to obtain different shapes tuning the wavelength where the maximum plasmon is located. Au bipyramids exhibit intense and well-defined plasmon resonance, easily tunable with the aspect ratio, and also strong localized electromagnetic field in the vicinity of the tips. Currently, our synthesis method leads to well-designed AuBPs in high yield and in high concentration, with a plasmon band located at 650 nm<sup>1</sup>.

Combining the ability to modulate the optical response of these NPs and to functionalize their surface with photosensitizers opens the way to new families of luminescent organic-inorganic materials. Synergy between Au NPs and chromophores has become a feasible way to control and modify optical effects<sup>2</sup>. This control and understanding of PS-NP interactions have attracted many scientists and a wide range of publications report the fluorescence quenching or enhancement of the photophysical properties of nearby molecules. The presence of a dye in the vicinity of a metallic surface can lead to the limitation in the dye photobleaching.

Rose Bengal (RB) is a metal-free, non-toxic, and popular PS that shows intense absorption bands in the green region of the visible spectrum (480-550 nm), and is renowned for its high quantum yield ( $\phi_{\Delta} = 0.76$ ) for the generation of <sup>1</sup>O<sub>2</sub>. In RB-NPs systems, it is now well established that the control of the dye-to-nanoparticle distance at the surface of the NPs is crucial to achieve the proper coupling between the plasmon resonance and the dye. RB needs to be located in a suitable distance ranging from 10 to 20 nm to achieve optimum emission enhancement according to literature. We have developed an easy method to control the distance between metallic surface and the photosensitizer with the SiO<sub>2</sub> thickness in order to increase the production of singlet oxygen. An enhancement has been shown for the obtained anisotropic RB@Au/mSiO<sub>2</sub> during photooxygenation model reactions in comparison with previous works<sup>3,4</sup>.

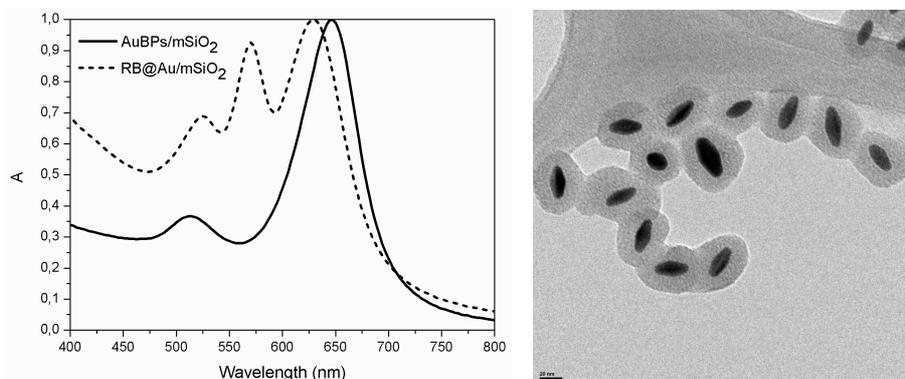


Figure 1. Left: Absorption spectra of Au/mSiO<sub>2</sub> and RB@Au/mSiO<sub>2</sub> nanobipyramids Right: TEM of RB@Au/mSiO<sub>2</sub> nanobipyramids

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# Dichroic surface plasmons in Au and Au-Pd nanoparticles: reactivity towards gas molecules and application to high-performance H<sub>2</sub> sensing.

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Gold nanoparticles (NPs) are of great interest for multiple applications, including their reactivity to catalytic reactions, as well as localized surface plasmon resonances (LSPRs), which can be excited by incident light. It is well known that the LSPR depends on a number of parameters, such as the size and shape of the NPs, the local environment and its interaction with them. In particular, the presence of molecules adsorbed on the surface of the Au NPs can induce a modification of the refractive index of the immediate environment, but also can be accompanied by charge transfers, which both strongly influence the wavelength position of the LSPR<sup>1</sup>.

Therefore, the study of the LSPR changes of Au NPs placed in a gas makes it possible to follow the presence and the adsorption of the gas molecules on the NPs. However, the reactivity of the Au, even with nanometric scale, remains low, leading to very small displacements of the LSPR, which can be much less than 1 nm and therefore hardly measurable. Here, we use a very sensitive optical surface technique, known as reflectance anisotropy spectroscopy<sup>2</sup>, to study such minute changes in the LSPR. The anisotropic samples of Au are formed of nanoparticles elaborated by oblique angle evaporation on a glass substrate, leading to dichroic NP films showing two different plasmon resonances as a function of the polarization of the light (Fig. 1).

We have applied this approach to several studies. (i) In order to demonstrate the performance of the method, we first studied its sensitivity to detect very small variations in the refractive index of the environment (water with alcohol). (ii) We conducted a comparative study of the adsorption of dioxygen and dihydrogen on Au NPs. The experiments were well reproduced by calculation, demonstrating the existence of charge transfers between the gold and the adsorbed entities<sup>3</sup>. (iii) By adding palladium to gold, we developed Au-Pd NPs to detect small amounts of H<sub>2</sub> in a carrier gas, showing that this method holds great promise for the development of highly sensitive plasmonic H<sub>2</sub> sensors (fig 1).

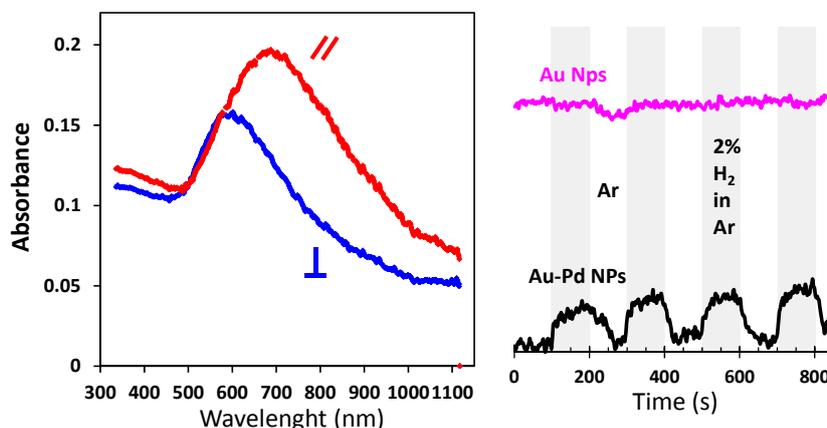


Figure 1. Left hand side: Absorbance of the anisotropic Au NPs film for two perpendicular polarizations of the light with respect to the direction of evaporation. Right hand side: Optical anisotropic signal measured during cycles of 2% H<sub>2</sub> in Ar vs. pure Ar, for Au and for Au-Pd NPs.

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# Plasmonic waveguide self-assembly on DNA origami

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The field of plasmonics exploits the interaction of light with nanoscale metallic structures to confine, guide and manipulate light on scales below the diffraction limit, thereby greatly benefiting applications such as quantum photonics, or short-distance optical communication. For example, deep subwavelength plasmonic waveguides fabricated from closely spaced metal nanoparticles have been proposed two decades ago, and were realized by electron beam lithography, a method which is, however, non-scalable. Moreover, it is desirable to attain a more precise control over the metal particle crystallinity, shape, size, positioning and interparticle spacing than that achievable by lithography. To this end, DNA nanotechnology can be used to self-assemble plasmonic structures with superior control. We systematically studied the assembly yield of gold nanoparticles on DNA origami structures as a function of a wide range of parameters such as ionic strength, stoichiometric ratio, oligonucleotide linker chemistry, and assembly kinetics by an automated high-throughput analysis of electron micrographs of the formed heterocomplexes.[1]

Next, we demonstrate energy propagation towards a fluorescent nanodiamond through a nanoparticle waveguide, and thus visually demonstrate the realization of nanometer-precise light manipulation. High-resolution mapping by electron energy loss spectroscopy and cathodoluminescence imaging spectroscopy reveal an efficient in-coupling, propagation and out-coupling of the energy over a distance of 350 nm. Finite-difference time-domain simulations reveal that several plasmon modes contribute to efficient waveguiding. We anticipate that combining DNA origami deposition, interfacing methods, and established microfabrication techniques with our scalable self-assembly approach will enable the construction of complex sub-diffraction plasmonic devices for applications in information technology, sensing and quantum optics.[2]

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# Near-Field Localization of Au Nano-objects: PEEM and Group Theory Description

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Localised surface plasmon resonances (LSPRs) are coherent and collective oscillations of the conduction electrons in metallic nanoparticles (NPs) under the influence of an external electromagnetic field. The resonance wavelength depends on the nanoparticle characteristics, the external environment and the illumination geometry.

In this work, the optical response of various metallic nano-objects of different geometries and sizes, taken individually: triangles [1], cubes [2], hexagons,... or in groups: dimers (bowties), chains... are studied by PhotoEmission Electron Microscopy (PEEM), a non-intrusive and high resolution (20nm) mapping technique allowing a selective addressing of plasmon modes. The LSPRs are excited by a femtosecond pulsed laser source operating in the visible and near IR wavelength ranges, and the polarisation is adjusted with a half-wave plate.

In addition to the experimental investigation, the search for a specific optical near-field distribution is also carried out using group theory, an original theoretical method allowing to predict the results in just a few minutes. Further theoretical support is obtained by *boundary element method* (BEM) numerical simulations.

To illustrate our investigation, figures (1.a) and (1.b) display the experimental and numerical dipolar signatures of a subwavelength sized nanocube under grazing incidence in *p* polarisation. These results show a good agreement between experiment and group theory. Taking into account the object symmetry, the near-field distribution can be interpreted as a combination of two dipolar modes, one excited by an electric field component normal to the cube upper face and a second one excited by the in-plane electric field component parallel to the same face (figure (1.c)). Any change in the light polarisation modifies the near-field optical distribution, so we can selectively address NP plasmon modes by changing the polarisation of the incident light.

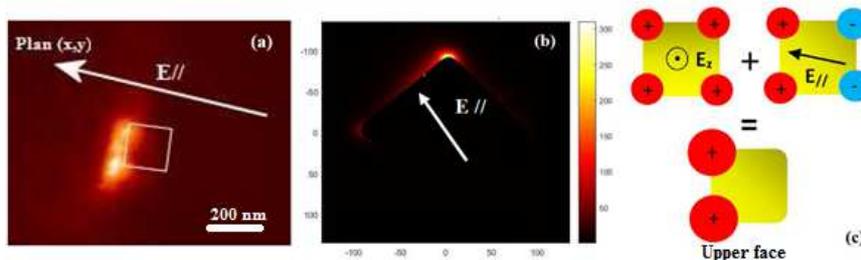


Figure 1. Near optical field mapping (a) PEEM (b) BEM simulation (c) Interpretation within a group theory approach.

To sum up, the plasmonic response of nano-objects depends strongly to the polarisation of the incident light and the object symmetry. Near field distribution of NPs of subwavelength size can be predicted within a group theory approach.

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# Multistructured metallic substrate as a new SERS platform : experimental studies and electromagnetic modeling of localized plasmon surface

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Since the first observation of Surface Enhanced Raman Scattering (SERS) in 1974<sup>1</sup>, a variety of methods have been developed to control physically the arrangement of metallic nanostructures onto a surface in order to enhance Raman signals. It is now generally believed that the magnitude of the SERS enhancement factor is mainly driven by the enhanced local electromagnetic field in nanostructured metal surfaces<sup>2</sup>. Previous studies revealed that gaps between adjacent nanoparticles or roughness give rise to strong enhancement effects, often referred to as 'hot spots'.

In 2014, we patented a force-assisted Atomic Force Microscopy lithographic method<sup>3</sup> allowing fabrication of reproducible metallic nanostructures with various shapes and sizes on the same substrate that can be solid or flexible.

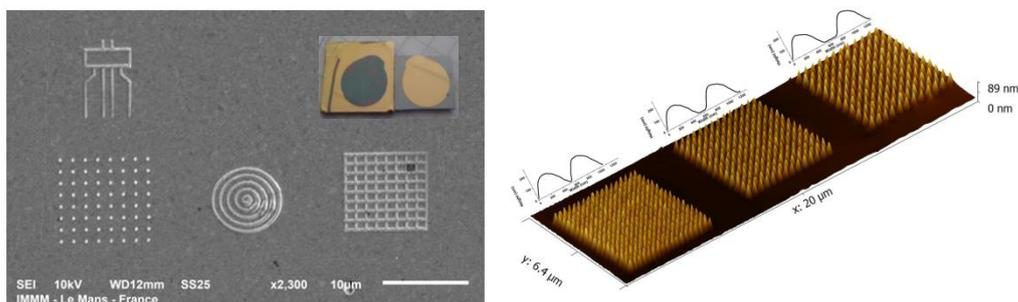


Figure 1. SEM and AFM pictures of various gold nanostructures

In order to investigate the relationship between nanostructures network geometry and spectral dependency of the local field enhancement, plasmonic response of nanostructures has been simulated using COMSOL Multiphysics®.

Localization of hot spot has been experimentally confirmed with Photoemission Electron Microscopy measures on different nanostructures and we also studied the SERS efficiency of our substrates by analyzing the Raman signal after immersion in diluted solution of Benzenethiol ( $10^{-6}$ ).

This kind of multistructured substrate opens the way for new theoretical and experimental fields in order to study and optimize physical mechanisms involved in SERS phenomenon.

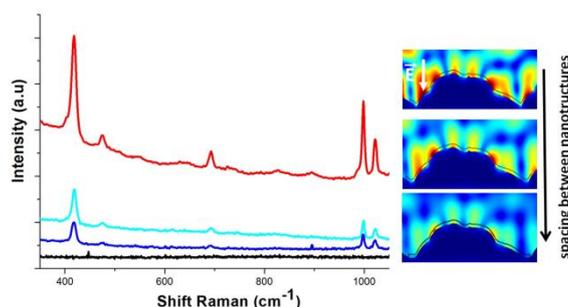


Figure 2. Raman spectra and local field calculation on various gold nanostructures

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# Local optimization of nonlinear luminescence in disordered gold metasurfaces by far-field wavefront control

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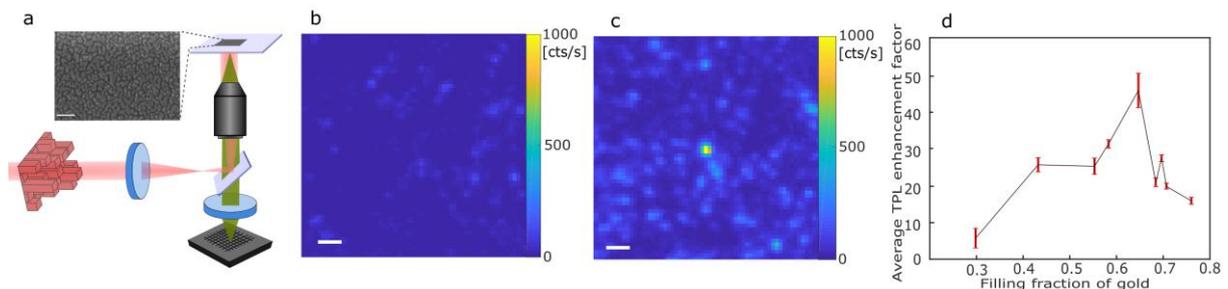
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Engineering the wavefront of light in random media allows the control of wave propagation in space and time by exploiting the spatial and spectral degrees of freedom introduced by multiple scattering.<sup>1</sup> To apply this far-field control strategy and focus electromagnetic energy at the nanoscale, it is necessary to introduce scatterers that feature strongly enhanced and confined optical fields such as plasmonic nanoantennas. In particular, semi-continuous gold films close to the percolation threshold feature high local field enhancements<sup>2</sup> but also propagating surface plasmon waves that can be controlled using a spatial light modulator.<sup>3</sup>

In this presentation, we demonstrate how controlling the phase of an incoming femtosecond pulsed laser on a chosen area of a disordered plasmonic metasurface allows us to optimize the two-photon luminescence (TPL) of gold at a given position of the sample. In practice, the incoming wave is shaped by a spatial light modulator (SLM), which is conjugated to the sample surface (see Figure 1-a). This provides us with a full control of the phase of the EM wave on the metasurface while maintaining a uniform illumination. Figure 1-b is a typical example of a widefield TPL image when exciting a plasmonic surface (gold filling fraction of 0.6) with a random phase pattern. The TPL signal originating from the center of the 35  $\mu\text{m}$  x 35  $\mu\text{m}$  phase pattern is optimized using a random iterative process as demonstrated in Figure 1-c.

The optimized TPL intensities are increased by an average factor of 50 for disordered gold metasurfaces that are close to percolation (see Figure 1d). When the filling fraction of gold is far from percolation, the enhancement factors decrease dramatically, demonstrating that the morphology and level of disorder of the plasmonic surface play an essential role in the wavefront control of nonlinear luminescence. Furthermore, we show that TPL intensities can be enhanced at any position of a percolated film. Since the TPL intensities are associated with strong local field enhancements, these results open exciting perspectives for the wavefront engineering of plasmonic hot-spots in disordered gold metasurfaces.



**Figure 1.** (a) *Excitation and imaging setup.* The gold metasurface (scale bar = 100 nm) is illuminated by a wavefront controlled femtosecond pulsed laser while the TPL signal is observed in full field with an EMCCD camera. Typical TPL image of the excited plasmonic metasurface before (b) and after (c) iterative optimization (scale bar = 2  $\mu\text{m}$ ). (d) *Average TPL enhancement factor as a function of the gold filling fraction of the plasmonic metasurface.*

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# Engineered protein-driven synthesis and assembly of hybrid nanoplasmonic superstructures

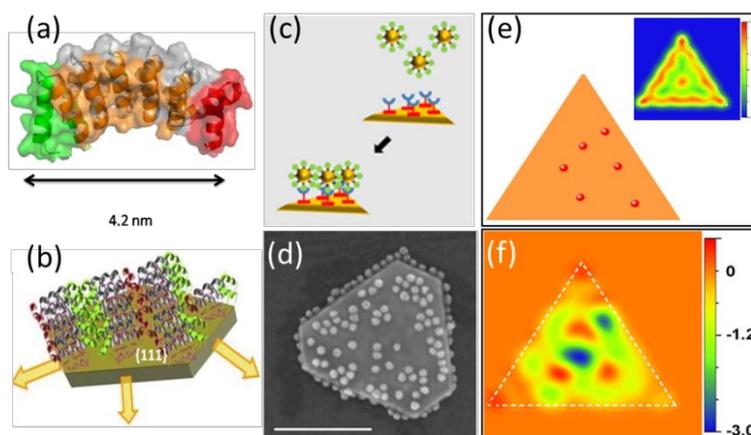
Laureen Moreaud<sup>1,2</sup>, Janak Prasad<sup>1</sup>, Upkar Kumar<sup>1,2</sup>, Sebastien Viollet<sup>3</sup>, Agathe Urvoas<sup>3</sup>, Cecile Marcelot<sup>1</sup>, Marie Valerio-Lepiniec<sup>3</sup>, Philippe Minard<sup>3</sup> and Erik Dujardin<sup>1</sup>

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The coupling of single emitters and plasmonic nanostructures promises attractive solutions for nanophotonics circuitry. Such systems provide improved luminescence, foster directional and tunable energy transfer in compact devices and is considered as a viable approach to Quantum Technologies. We have recently demonstrated that transmission and computation channels in plasmonic structures can be designed by spatially and spectrally tailoring the plasmon local density of states (SPLDOS).<sup>1-3</sup> Yet the exploitation of such functionalities demands to overcome the challenge of placing single emitters at predetermined sites of a metallic nanoparticle where they can act as integrated point light sources or optical two-level systems. Here, we show a new and generic bottom up approach using purpose-designed Au(111)-binding artificial proteins to grown plasmonic Au nanocrystals. The involvement of proteins in the morphosynthesis process is demonstrated by the exclusive presence of Au (111) facets in all nanocrystals. Furthermore, the proteins form a strongly bound capping layer that can be easily functionalized.<sup>4-6</sup> These crystals are decorated with robust emitters such as gold clusters, nanodiamonds and core-shell quantum dots. The hybrid structures are structurally and optically characterized by microscopy and spectroscopy techniques. Ultimately, our approach combined to plasmon-driven chemistry will enable the control of the localization of the emitters on the surface of the metallic particles in order to address a single mode borne by the plasmonic cavity and operate transmission devices.<sup>1,3</sup>



**Figure 1:** Schematic shows (a) helicoidal repeats in alpha-rep, (b) alpha rep directed crystal growth and (c) assemblies of nanoparticles on gold platelets. (d) SEM image of (c).<sup>6</sup> (e) Model of assemblies between nanoprism and randomly adsorbed particles, LDOS map at 683 nm insert. (f) 2D maps of the LDOS difference between (e) and LDOS map without particles.<sup>5</sup>

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# Gold films with subwavelength holes: Optical properties in the scope of nonlocal charge carriers

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Electron-electron interactions in metals are neglected in classical electrodynamics. Though short-ranged, it was shown that they have a remarkable impact on the optical response of metal nanoparticles [1-3].

Two-dimensional, subwavelength hole arrays in metal films are equally a source of nonlocal electron dynamics [4,5]. We discuss the impact of spatial dispersion in plasmonic crystal films using the generalized hydrodynamic approach [2,5] extending established periodic crystal concepts [4,6,7].

The excitation of additional pressure waves and anomalous diffraction lead to a substantial change in the bandstructure and electromagnetic fields supported by a nonlocal holey metal film with respect to the classical local response approximation, see Fig. 1, even at large geometrical parameters. In contrast to homogeneous nonlocal metal films [8], spatial dispersion emerges also at normal incidence.

This impacts many concepts and applications in photonics such as imaging and extraordinary optical transmission (EOT) and we aim to enhance the understanding of spatial dispersion in promising building blocks for photonic circuits, bio-chemical sensing and spectroscopy.

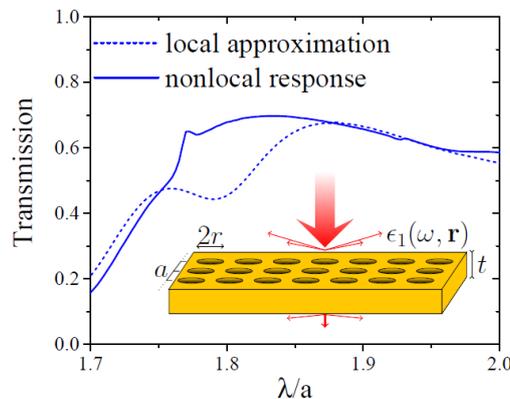


Figure 1. Extraordinary optical transmission in holey gold films in classical electrodynamics (dotted) and beyond local nanophotonics (solid). The lattice period is 400 nm, the air hole radius 100 nm and the film thickness 20 nm. The gold film is suspended in air and illuminated at normal incidence.

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# Nanograting for lasing action and sensing.

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**Abstract:** One of the most exciting and recent use of metallic nanograting is as a plasmon laser. Such laser has been demonstrated recently theoretically and experimentally at room temperature.<sup>1,2,3</sup> In this conference we will present our latest results on Plasmon based laser. We will investigate the near field properties of the demonstrated plasmon-based laser. We demonstrate that due to the coupling between gain molecules (Rhodamine) and a lattice plasmon mode we could achieve a much higher enhancement of electromagnetic field as compared to the passive structure (no gain media) (Figure 1). We will demonstrate that the near field enhancement in such laser has a non linear behavior as a function of the pumping rate. We will discuss the application of such properties in sensing.

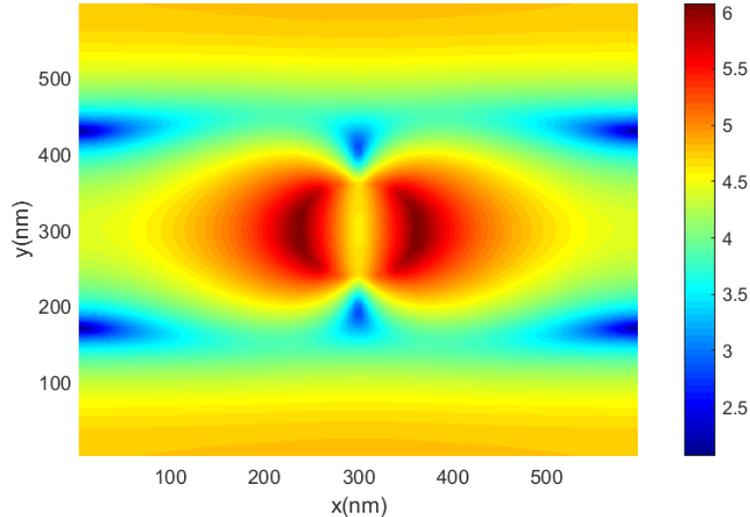


Figure 1: Plasmon-based laser: Optically pumped, 2D arrays of plasmonic Au nanoparticles surrounded by an organic gain medium exhibits a high enhancement field above the threshold of lasing (*log scale*).

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**Ref3:** Yang A., Young. T, Dridi M., Real-time Tunable Lasing from Plasmonic Nanocavity Arrays. *Nature Communications*

# Gold nanoantennas for optical excitation of spin waves

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Presently the coherent excitation of spin ensembles using plasmonic structures is of prime research importance since it potentially can expand the functionalities of magnonics. In this work, gold nanodisks deposited by electron beam lithography on magnetic films are investigated, and the optical properties of the resulting samples were studied by simulations and measuring the transmittance and magneto-optical effects.

To date, the latest achievements of science and technology have led to the possibility of creating a new functional magnetic structures of various designs, which have modified optical properties, with characteristic dimensions in the order of several tens of nanometers. Such nanostructures allows to control the characteristics of optical radiation at a scale smaller than the wavelength of light. The effectiveness of this control is achieved mainly by nanostructuring materials<sup>1</sup>, which enables to create a medium with predetermined optical properties and enhance the optical and magneto-optical effects by only optimizing the geometric structure. Plasmonic nanostructures are gold nanoparticles (nanodisks) with characteristic dimensions such as diameter of 50-150 nm, height ~ 50 nm and a period of 80-500 nm deposited on a magnetic dielectrics. Bismuth rare-earth iron garnet is used as a magnetic dielectric. Gold nanodisks dimensions must be chosen in such a way that the femto-second laser pulse excites the localized surface plasmon polaritons (LSPP). Upon excitation the LSPP significantly increases the intensity of the magnetic field near the nanodisks, which in turn increases the value of the inverse Faraday effect, which is directly proportional to the intensity of electromagnetic radiation. This is an increase of the effective magnetic field near nanodisks. Consequently, nanodisks can operate as local sources of magnetostatic spin waves, which excited, usually, the magnetic field of the microwave radiation generated by the antenna in the vicinity of the sample<sup>2</sup>. However, in a number of important applications it is required to excite spin waves locally and there is a need to create a certain spin density distribution in space and time. A key factor in this work is the excitation of LSPP at a certain wave, you need to correctly calculate the nanoscale structures using electromagnetic simulation. To investigate the electromagnetic field distributions induced by surface plasmons, we performed the numerical calculation based on the rigorous coupled-wave analysis method (RCWA). The results of the work are parameters of two-dimensional gold lattice of nanodisks and calculated field of the inverse Faraday effect which is compared with the case without gold and the case of smooth gold on the surface of the iron garnet. Parameters of structure are optimized for effective excitation of LSPP at a wavelength  $\lambda = 820$  nm - a wavelength of a Ti: sapphire laser. The work was supported by the Russian Science Foundation (RSF) (17-72-20260).

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# Plasmonic nanorattles via galvanic replacement-seeded growth method: Towards a Universal SERS Tag

S. Rodal-Cedeira<sup>1</sup>, S. Bals,<sup>2</sup> J. Pérez-Juste<sup>1</sup> and I. Pastoriza-Santos<sup>1</sup>

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Control over the morphology of metal nanoparticles (NPs) in combination with mechanistic understanding is a crucial step for the development of modern nanoscience and nanotechnology. Nanoscale galvanic replacement reaction has been widely used as a convenient approach for the transformation of solid NPs into corresponding porous/hollow NPs, in which pore size and chemical composition controls their optical and catalytic properties. Galvanic replacement reaction on Au@Ag core-shell NPs lead to the formation of nanorattles with complex chemical composition, while preserve the morphology of sacrificial template. The internal electromagnetic hot spots of plasmonic nanorattles make them ideal for plasmon-enhanced applications. Recently, the three-dimensional (3D) morphological and chemical architectural transformations associated with the formation process of nanorattles were revealed by quantitative EDX tomography technique for simultaneous elucidation of 3D morphological and chemical architectural transformations involved during the transformation.<sup>1</sup> The presence of reducing agent lead to such unconventional mechanistic path, in which galvanic replacement dominates in the initial stages of the reaction, while overgrowth suppress the dealloying process in the later stages of the reaction.

Herein we demonstrate that in the presence of high gold salt concentrations the overall process lead to the formation of closed hollow plasmonic nanoparticles. Interestingly, the addition of different molecules during the synthesis of the nanorattles lead to its encapsulation within the inner void. This approach allowed us to codified the plasmonic particles with a library of Raman active molecules leading to the formation ultrasensitive SERS-encoded nanoparticles.

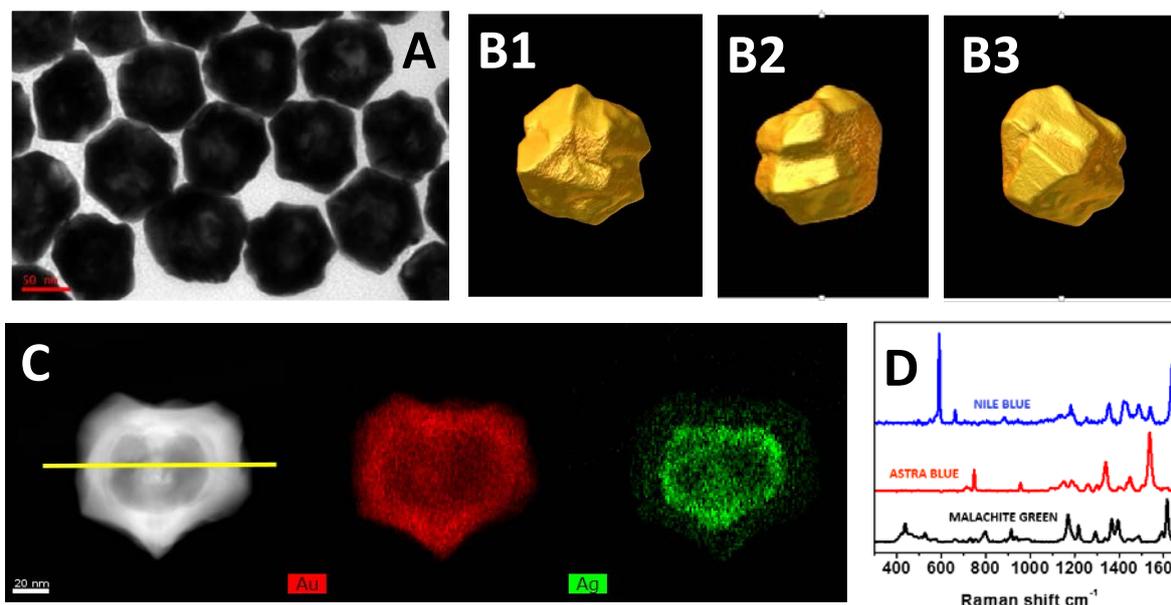


Figure 1. (A) Representative TEM image of the closed Au nanorattles. (B) 3D visualization of the tomographic reconstruction along different views of an Au nanorattle. (C) SEM images of the hierarchical nanoparticles assembly (C) STEM image and EDX mapping showing the Au and Ag distribution. (D) SERS spectra of different Au nanorattles encoded with several Raman reporters as indicated..

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# Plasmon-mediated remote Raman of coaxial nanowires

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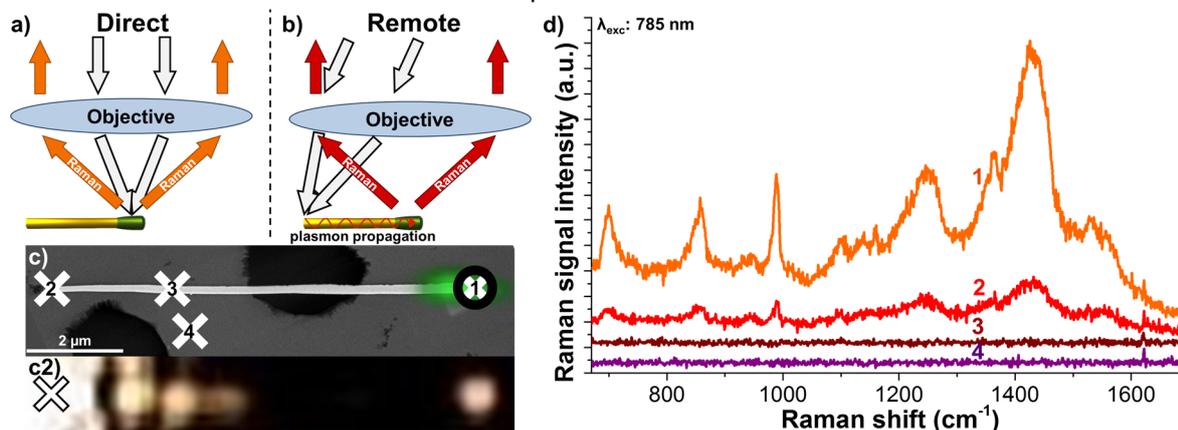
The combination of localized surface plasmon resonance (LSPR) and surface plasmon polariton (SPP) effects in 1D hybrid nanostructures is a recent domain of investigation and it is particularly promising for the remote sensing of different species [1]. Besides applications in nano-sensors, the remote emission is also of great interest for nanophotonics as it combines nanowaveguiding and nanosources.

The unusual “remote” geometry for Raman study is based on the laser excitation of the SPP at one tip of the nanowire and the probing of the Raman signal at another position separated by several micrometers from the excitation laser spot (Figure 1 (a) and (b)). Thus, it requires to tackle the following challenges: efficient injection coupling, long-enough nanowires to prevent parasitic “direct” Raman signal coming from the excitation area, low plasmonic losses of the SPP, efficient coupling of the SPP with the Raman scatterer species to detect. The very weak efficiency of Raman scattering makes it particularly challenging in a remote configuration.

In this study, we designed different kinds of coaxial nanowires, asymmetric or not, and we explored their remote-Raman behaviour. A gold core nanowire for SPP surrounded with a poly(3,4-ethylenedioxythiophene) shell, a conjugated polymer as Raman scattering system, serves as a platform for our investigations. The improved hard template-based process allowed to control, not only the nanowire diameter (between 20 to 200 nm) and length (up to 20 micrometers), but also the location of the conjugated polymer shell: only at one nanowire tip (Figure 1(c)), all along the nanowire, at the two nanowire tips. Remote-Raman effects were demonstrated unambiguously for nanowire length up to 9  $\mu\text{m}$  (Figure 1(d)).

The effect of the excitation wavelength (488, 514, 633 and 785 nm) on the direct and remote Raman spectra was determined: (i) the lack of Raman signal in the remote geometry for 488 and 514 nm was attributed mainly to the SPP losses in gold, (ii) the spectra measured in remote geometry strongly depends on resonant Raman scattering for the pi-conjugated polymer, (iii) the huge variation of the measured spectra with the polarization of both the excitation laser and the scattered remote-Raman signal has been attributed to the efficiency of SPP excitation and to the strong ordering of PEDOT chains promoted by the ultra-confined synthesis configuration.

Our results give new insight in the physics of this complex but promising phenomenon. The original coaxial nanowires are candidates for developing remote nanosensors. Furthermore, we are developing new nanowire architectures to enhance this phenomena.



**Figure 1.** Schematic view of the optical configuration (laser source, objective, sample and collected light) for measuring the standard (a) and the remote (b) Raman signals. (c) Scanning electron microscopy image with superposed Raman spectroscopy mapping (intensity at  $1430\text{ cm}^{-1}$  appears green) of a single gold nanowire (diameter: 114 nm) covered with PEDOT only at the right tip. Four excitation configurations (X symbol labelled 1 to 4) and maintained collection area (O) of the Raman signal plotted in (d) at 785 nm. (c2) Optical microscopy image without back light when exciting in position 2 with a 785 nm laser.

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# SERS improvement by a gold reflective underlayer and localised detection of thiophenol by SFG for gold nanotriangles

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Firstly, we report on an improvement way of the SERS signal of Au nanotriangles for a highly sensitive detection of chemical molecules. This improvement is obtained by a simple addition of a gold reflective layer under Au nanotriangles. Using the same Au triangular nanoprisms obtained by nanosphere lithography (NSL) (see figure 1(a)), we studied experimentally the thickness effect of this gold underlayer on the SERS intensity of the gold nanotriangles. We demonstrated that this SERS intensity increased with the thickness of the gold reflective underlayer (see figure 1(b)), and this is due to the increment of the Au underlayer reflectivity. Indeed, enhancement factors of  $10^8$  were found for the most important thickness of the gold underlayer<sup>1</sup>. Secondly, with these same structures with a gold underlayer thickness of 30 nm, we detected two vibrational modes of thiophenol molecules localised on the lateral sides (walls) of the nanotriangles by using the Sum-Frequency Generation (SFG) spectroscopy (see figure 1(c)). Raman shifts of these two modes are 3050 and 3071  $\text{cm}^{-1}$ , whereas they are usually very difficult to distinguish by SERS and other vibrational optical probes. In the *ssp*-configuration of our SFG setup, these vibrational modes have been detected thanks to the excitation of a transversal plasmon mode by the incident visible laser beam<sup>2</sup>.

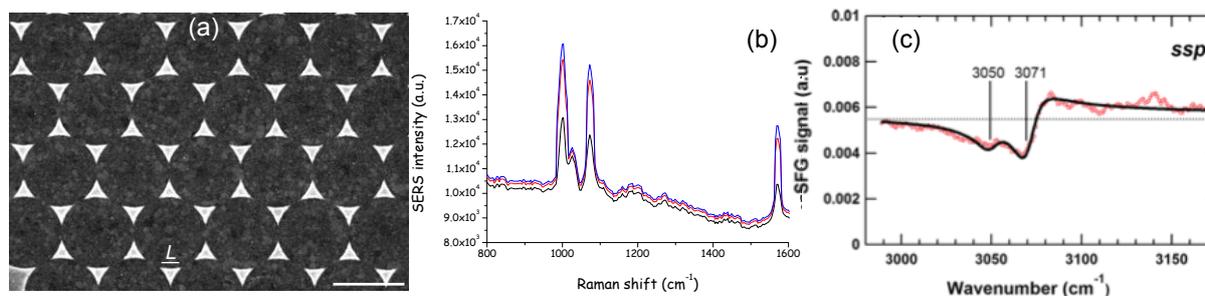


Figure 1. (a) SEM image of gold nanotriangles on a gold film obtained by NSL (scale bar = 500 nm), (b) SERS spectra of thiophenol molecules obtained with gold nanotriangles for 3 different thicknesses of the underlayer (black = 30 nm, red = 50 nm and blue = 100 nm), and (c) SFG spectrum of thiophenol molecules obtained with the gold nanotriangles on a gold film of a 30 nm-thickness in *ssp*-polarisation configuration of our SFG setup for an incident visible beam wavelength of 532 nm.

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# Designing small aggregates of nano-particles by AFM to generate tunable Resonant Raman structures.

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Our group develops a new approach combining an Atomic Force Microscope and a confocal-Raman microscope [1], where AFM microscope is used to image and to manipulate nano-particles under the confocal optical microscope coupled at the Raman spectrometer. Our optical device allows us to scan the resonance effects by tuning the wavelengths of excitation.

This talk will show the results obtained with some symmetric structures of assembling of gold nano-particles (AuNPs), in the vicinity of a single and isolated carbon nanotube (CNT). We will investigate the consequence on the super-resolved Raman spectra and as a function of the different sub-wavelength-scale geometries of AuNPs aggregates. We will discuss the different interactions between AuNPs aggregates and the nano-carbons, including their impact on resonance effects. In particular, we will focus on the enhancement of the local electrical field by metallic nano-structures to probe single objects.

These experimental data are interpreted according to finite element models (Figure 1) of far and local electromagnetic fields. Thus, on one hand, we achieve to a better understanding about the tunability of plasmon resonance modes of home-tailored nanostructures, including sensitive breaks symmetry modes. On the other hand, the consequences of their interactions with a substrate or molecule dipole moment, depending on the excitation wavelength (especially in the case of the inelastic scattering) [2], are studied. All this allows us to understand and predict the experimental observation (see Figure 1).

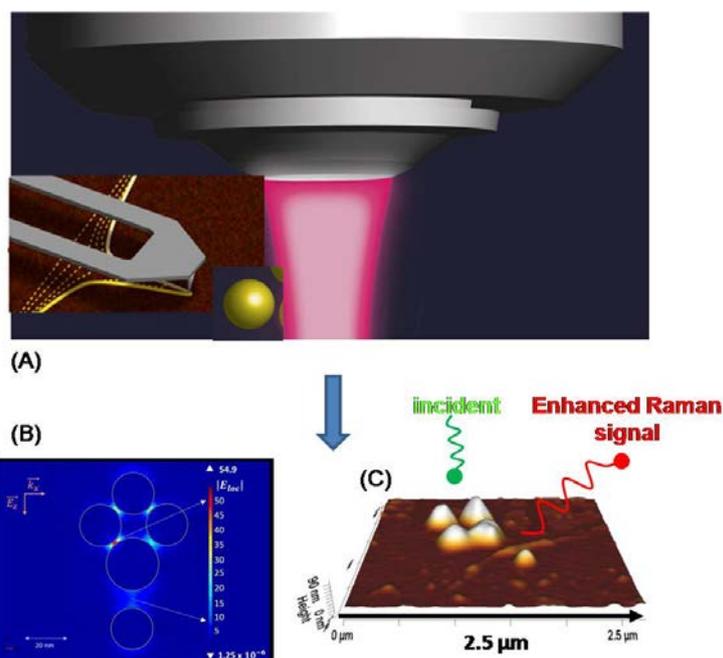


Figure 1. Gold nano-assembly by AFM manipulations (A) to create a nanostructure able to enhance local electric fields under excitation, as predict in the FEM computations (B) and measured experimentally (C).

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# Tip-enhanced Raman spectroscopy to distinguish toxic oligomers from A $\beta$ (1-42) fibrils at the nanometer scale

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Tip-enhanced Raman spectroscopy is a powerful technique combining the high sensitivity of surface-enhanced Raman spectroscopy (SERS) and the nanoscale lateral spatial resolution of scanning probe microscopies, such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM). AFM-TERS has been already employed to achieve nanoscale chemical characterization of biochemical and biological samples.<sup>1</sup> However, analyzing amyloid fibrils, consisting of  $\beta$ -sheet-rich peptide aggregates, using TERS remains a challenging task<sup>2</sup> since the spectral fingerprint of the peptide secondary structure, namely the amide I band, can be missing in amyloid TERS signatures.<sup>3</sup>

Here, natural A $\beta$ (1-42) fibrils (WT) implicated in Alzheimer's disease as well as two synthetic mutants forming less toxic amyloid fibrils (L34T) and highly toxic oligomers (oG37C) are chemically characterized at the scale of a single structure (~30 nm) using tip-enhanced Raman spectroscopy (TERS). While the proportion of TERS features associated with amino acid residues is similar for the three peptides, a careful examination of amide I and amide III bands allows us to clearly distinguish WT and L34T fibers organized in parallel  $\beta$ -sheets from the small and more toxic oG37C oligomers organized in anti-parallel  $\beta$ -sheets.<sup>4</sup> This work opens promising perspectives for the detection of pathological species.

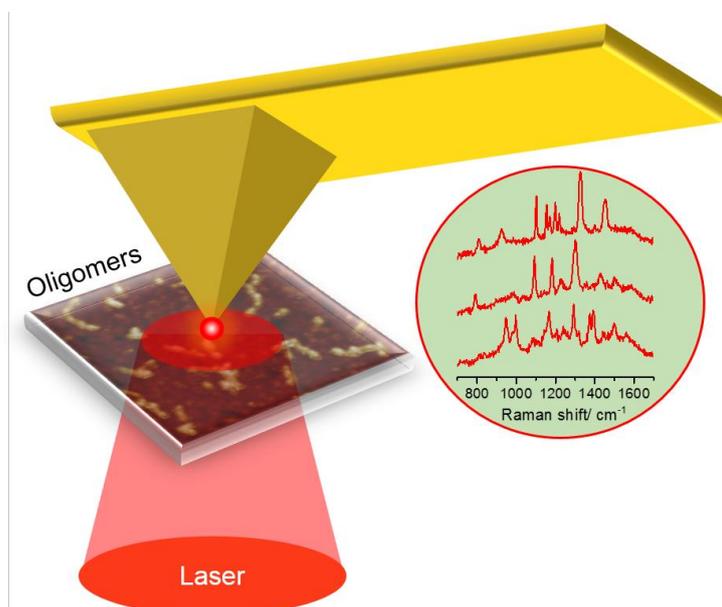


Figure 1. AFM-TERS configuration under 633 nm irradiation and a few TERS spectra observed for toxic oligomers.

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## TERS characterisation of 2D materials

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Ultimate device miniaturisation is coming with the emergence of atomic layer electronic materials. The development of these 2D materials based nanodevices requires characterisation of structures at the nanoscale. Tip Enhanced Raman Scattering (TERS) is now the ideal tool as it provides chemical, topography and electrical information at the same location with nanometer spatial resolution [1-3]. TEOS (Tip Enhanced Optical Spectroscopy, including TERS and TEPL, Tip Enhanced Photoluminescence) allows to determine the number and orientation of layers, the quality of the materials, the presence of defects and their density, and the effects of strain or doping elements. Results of characterization of graphene, functionalized graphene oxide and 2D semiconductors ( $\text{MoS}_2$  (Fig.1) and  $\text{WS}_2$ ) will be reported. The capability of seeing deep-sub-diffraction-limited details correlated with complementary Kelvin probe microscopy and photo-current techniques will be demonstrated.

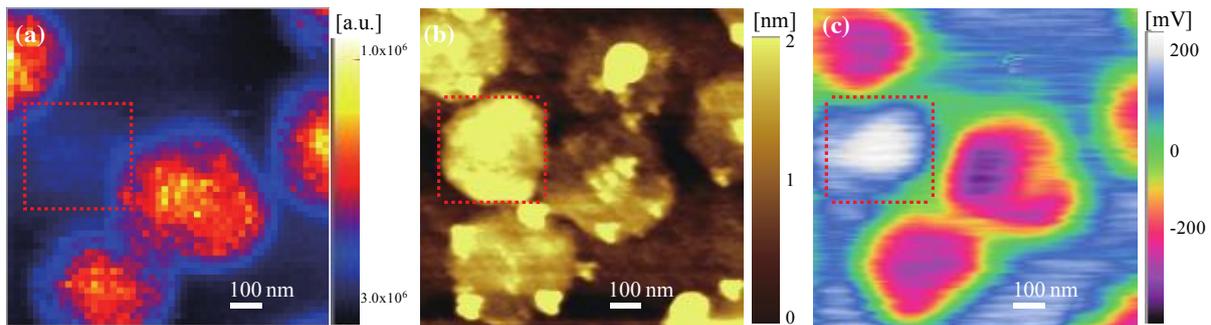


Figure 1. (a) TEPL map, (b) AFM image of monolayer and bilayer  $\text{MoS}_2$  flakes. Inset: line profile across both types of  $\text{MoS}_2$  flakes and (c) kelvin force image (same area as images (a) and (b)).

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# Optically directed assembly and non-reciprocal interactions of anisotropic gold nanoparticle ensembles

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Non-conservative forces have recently been postulated that could result in unusual dynamics of optically trapped plasmonic nanoparticle ensembles.<sup>1</sup> Studies of nanoparticle-based optical matter have focused on spherical constituents. Yet nanoparticles with other shapes are expected to have different local electromagnetic field distributions due to the increased significance of higher order (scattering) modes and therefore interactions with neighbors in optical matter arrays. One thus expect their dynamics to be different as well.<sup>2</sup>

We use quasi-1D optical trap to investigate the dynamics of asymmetric plasmonic ensembles (Au nanoplatelets, Au-nanostars, Au-clusters). We show that, when the symmetry of the light scattered by the nanoparticle ensemble or array is broken non-reciprocal interactions and non-uniform dynamics are induced. In the case of linear nanoplatelets arrays, it results into non-correlated motions on opposite sides of the arrays when there are unequal numbers of particles left and right of the optical trap center. For asymmetric clusters of nanoparticles, we observe driven motion of the particles that can push or pull on neighboring particles. Our findings demonstrate new opportunities to generate complex addressable optical matter and create novel active optical technology.

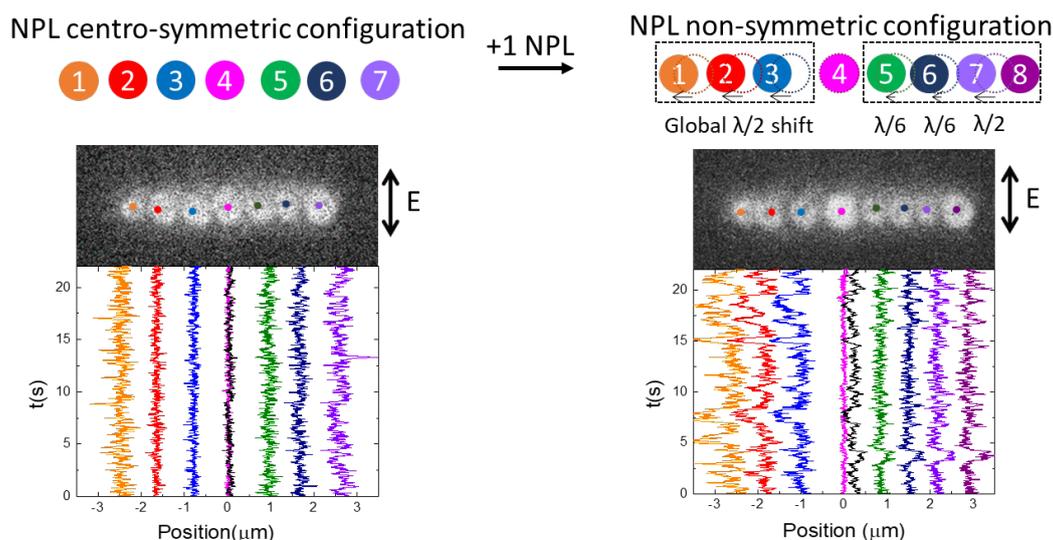


Figure 1. Gold nanoplatelets arrays in optical line trap: Dark field image and trajectories of each nanoplatelet. The black trajectories correspond to the calculated trajectory of the mean of each array.

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# DNA Origami Nanophotonics: Gold Optical Antennas for Fluorescence Enhancement and Diagnostics Applications

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In this contribution, we will focus on different applications of the DNA-Origami technique<sup>1</sup> in the fields of fluorescence enhancement and diagnostics. In particular, we employ DNA-Origami as a platform where metallic nanoparticles as well as single organic fluorophores can be organized with nanometer precision in three dimensions. We develop optical antennas (see Figure 1a) based on 100 nm Au nanoparticles with an interparticle gap of 12 nm. These self-assembled nano-antennas can reach a fluorescence enhancement of a factor 5000 and detect a single molecule at concentrations as high as 25  $\mu$ M, outperforming top-down lithographic nano-antennas<sup>2</sup>.

Furthermore, by incorporating silver nanoparticles, a fluorescence enhancement over a broader spectrum in the visible range can be obtained. We will show that dimer antennas based on 80 nm Ag nanoparticles can lead to an enhancement in the blue, green and red spectral region<sup>3</sup>. In addition, these antennas can also increase photostability reaching an enhancement of the average number of emitted photons before photobleaching of approximately 30<sup>4</sup>. We employ these optical antennas in order to develop hybrid-sensing assays in which we combine plasmonics with DNA walkers<sup>5</sup> and DNA hairpins<sup>6</sup>. Finally, we will discuss how these antennas can be integrated to reach single molecule sensitivity with smartphone-based devices (Figure 1b). These findings pave the way for the development of inexpensive point of care diagnostic platforms for the detection of pathogens at an early stage under condition of significant background such as blood or urine.

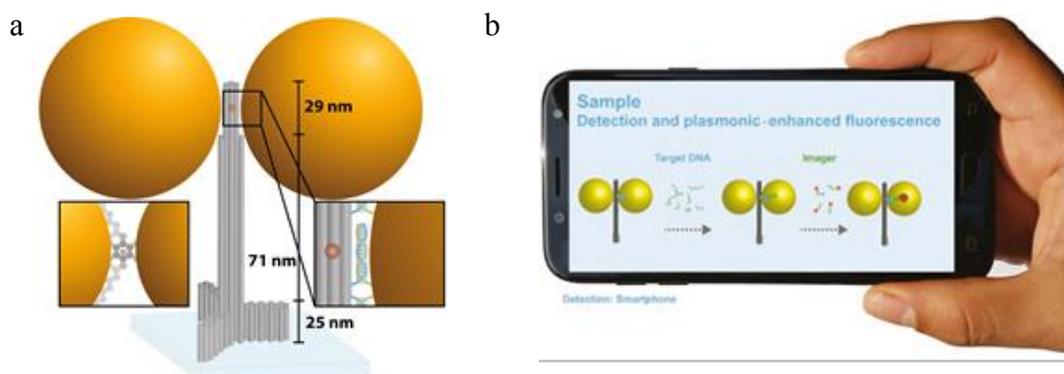


Figure 1. (a) Sketch of the DNA-Origami based optical nanoantenna dimer with two 100 nm gold nanoparticles and an immobilized fluorophore (ATTO647N) fluorophore at the hot-spot. (b) Sketch of a point of care diagnostic platform in which fluorescence arising from an optical antenna is detected by a smartphone-based fluorescence microscope.

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# Plasmonic biosensing using AuNP-bioconjugates with a smartphone-based spectrometer

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Portable spectroscopy is an emerging technology that holds great promise for biochemical sensing, food analysis and point-of-care testing. Standard spectrometers are typically restricted to Research activities due to their cost and complexity. Smartphone-based spectrometers are opening new paths to applications where ease-of-use, portability and cost-efficiency are key. When used in combination with functionalized gold nanoparticles whose spectrum changes in the presence of target molecules, they become powerful biosensing tools with numerous potential applications.

In this paper, we report on the localized surface plasmon resonance (LSPR) biosensing transduced by smartphones. As a proof of concept, we studied antibodies antigen interaction on gold nanoparticles (AuNP) bioconjugates. This system has been shown to lead to very specific and sensitive detection of toxins and allergens. A grating-based spectrometer was developed and adapted to a commercial smartphone. A mobile app was designed to acquire, save and compare spectra. The device has a resolution of 5nm and an accuracy of 1nm. It operates in the range of 400-700nm. This device successfully measured spectral shifts down to a few nanometers in the plasmon resonance of gold nanoparticles (AuNP). Upon antibodies attachment to the AuNP surfaces, an 8-nm shift was recorded, as shown in Figure 1, which perfectly matches with the values obtained using classical UV-Visible spectrometers. These preliminary results are therefore promising and should lead to a sensitivity and specificity comparable to that measured with classical equipment. The sensitivity and specificity of the response are currently under investigation.

A picture of the smartphone-based spectrometer and measured spectra are shown in Figure 1.

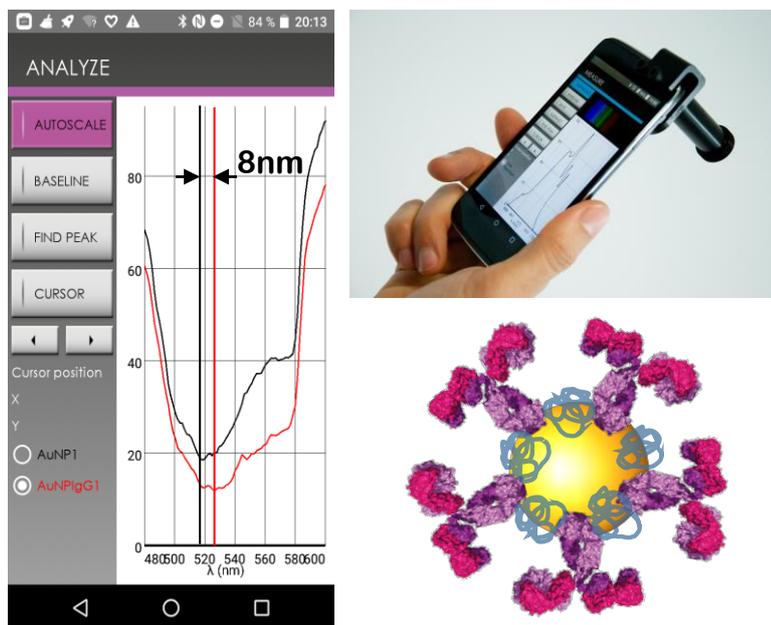


Figure 1. Measured spectra, smartphone-based spectrometer and AuNP bioconjugate

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# Microfluidic induced supercrystals for *on-chip* ultrasensitive SERS detection

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Microfluidic platforms allows generating a highly-ordered assembly of uniform gold nanoparticles inside their microchannels through the pervaporation of the solvent (Figure 1A-B).<sup>1</sup> Furthermore, the microfluidic approach enables the fabrication of uniform assemblies of any dimension or morphology. The resulting plasmonic devices could be used for the detection of analytes, even without affinity for gold nanoparticles.

Surface-enhanced Raman spectroscopy, SERS, is an advanced analytical technique that can be used for the ultrasensible detection of analytes since it offers orders of magnitude increases in Raman signals. It occurs at the surface of a plasmon surface mainly due to the presence of strong electromagnetic fields generated after the plasmon excitation. Moreover, this effect could be more intense in the case of hierarchical nanoparticles assemblies due to an antenna effect as demonstrated by recent simulations.<sup>2</sup>

While the plasmonic substrates made by drop-casting show poor uniformity that limits their potential plasmonic applications, the microfluidic approach gives rise to platforms with highly uniform and intense SERS activity (being both key parameter to achieve quantitative analysis and low detection limits (LOD)). Herein we will show the fabrication and characterization of plasmonic platforms fabricated using Au octahedra synthesized through a wet chemical method. Besides, the sensing capabilities of the platforms will be analyzed by investigating the SERS efficiency using different Raman active analytes. For instance, experiment performed with Malachite Green showed a great LOD, lower than 100fM, which is several orders of magnitude lower than those found in the literature.

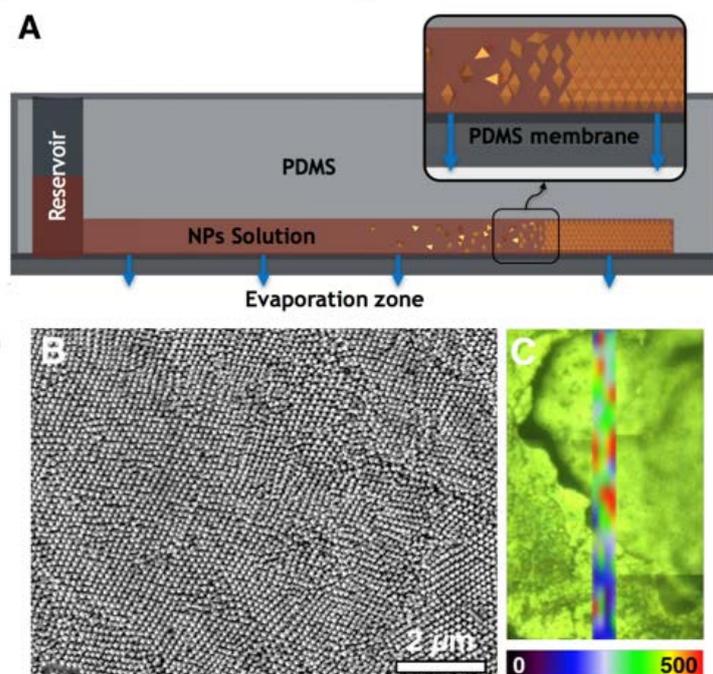


Figure 1. (A) Schematic illustration of the evaporation-based microfluidic cell used for controlled assembly of Au nanoparticles. (B) SEM images of the hierarchical nanoparticles assembly (C) SERS mapping of the channel in the presence of 100 fM of Malachite Green.

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# Detection of drugs metabolites: from the synthesis of tailored Au-based nanocomposites to SERS measurements

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The detection and assay of drugs and their metabolites at low concentrations in biologic matrices is a major societal issue and a major challenge in the analytical area due to the strong demand in fields such as pharmacology, toxicology, forensics, doping. At present time, this detection is performed using immunoanalysis and chromatographic techniques that have both their strengths and weaknesses. In this way, the analytical technique that is low-cost, rapid, simple, specific and highly sensitive does not exist yet. Raman spectroscopy has been envisaged for that purpose as it is a rapid, simple and low cost technique and it is also specific as it can discern compounds with similar structures. But, Raman scattering presents a small cross section. This main bottleneck was overcome with the discovery in 1977 of SERS effect. Even if a lot of compounds in wide concentration ranges were studied using SERS effect, the design of efficient and flexible nanostructured substrates for detection using Raman spectroscopy is still one of the main challenges to be achieved to ensure highly reproducible and large enhancement factors.

In this context, tailored Au-based nanocomposites were elaborated using an innovative procedure consisting in the preparation of preformed Au nanoparticles stabilized by amphiphilic block copolymers and their use as templates for the preparation of mesoporous silica loaded with these particles. Using this synthesis route, the size, the amount and the location of nanoparticles are controlled. After the determination of the textural properties of these nanocomposites, adsorption properties of Oxazepam, a benzodiazepine metabolite, were studied from a thermodynamic point of view via the construction of adsorption isotherms. In this way, it was possible to determine the Raman response of Oxazepam for known adsorbed amounts and thus, to evidence without any ambiguity SERS effect (see Figure 1). Finally, the drug Raman response was studied as a function of nanoparticles size and amount in order to understand the synergistic interplay between materials parameters/adsorption process and the drug detection threshold.

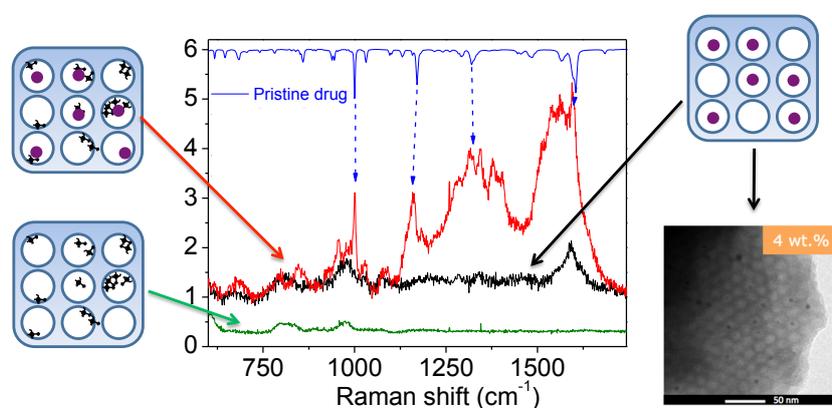


Figure 1. Raman spectra evidencing SERS effect for Oxazepam adsorbed on Au-based nanocomposite (TEM picture)

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# Dynamics in Small Metal Clusters

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The success of synthesizing monolayer protected clusters (MPCs) in the condensed phase has allowed scientists to probe their optical properties directly. Au MPCs have become the “gold” standard in nanocluster science due to the application of very rigorous chemical and structural characterization techniques. The use of ultrafast laser spectroscopy on MPCs in solution provides the benefit of directly studying the mechanisms of the dynamics of metal nanoclusters, and their non-linear optical properties. Based on the use of nonlinear and time-resolved spectroscopic techniques it is clear that monolayer protected metal clusters have unique physical and optical properties which are different than their larger metal particle counterparts. In this presentation the basic optical properties of metal clusters will be presented. Both linear and nonlinear optical measurements as well as steady state and time-resolved investigations of metal clusters will be presented. Applications of these clusters utilizing nonlinear optical methods will also be discussed.

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# Second Harmonic Generation from Nanocylinders : from a Single Nanocylinder to a Nanocylinders Array

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There has been in the literature an extensive study of the linear and nonlinear optical properties of metallic nanostructures. These works have principally focused on the origin of the response on the one hand and on the surface plasmon resonances engineering on the other hand. Nevertheless, some issues remain like the building of a coherent SHG response of an array of nanostructures from its individual constituent nanostructures.

To address this question, we have recorded the Second Harmonic Generation intensity of individual gold nanocylinders forming a square array, see Figure 1. This study has been performed as a function of the input polarization angle in order to generate polarization resolved plots of the SHG response. A common bias towards a defined polarization direction is detected for each single nanocylinders, suggesting that SHG is a perfect tool to assess the quality of a metallic nanostructures array. Besides, this study also indicates that the origin of the SHG response of the nanocylinders stems from shape defects breaking the centrosymmetry of these otherwise centrosymmetric nanostructures.

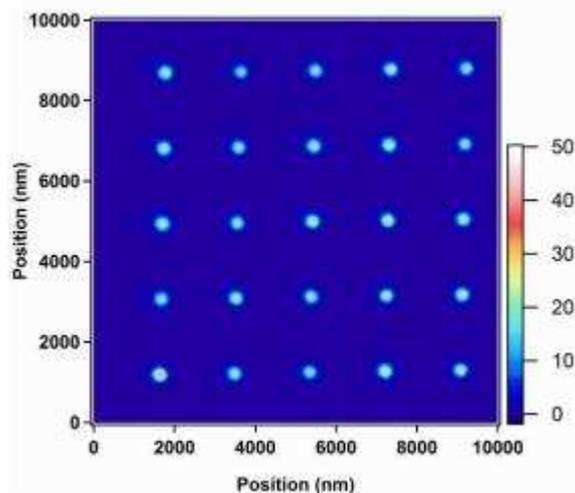


Figure 1 : SHG Intensity map of an array of 100 nm diameter gold nanocylinders.

In a second step, we have observed the SHG response from a square array of the gold nanocylinders. The overall response of the array presents a similar bias towards the same defined input polarization direction as the individual nanocylinders, resulting from the superposition of the individual gold nanocylinders response. Also, due to the origin of the response, no coherent response may develop in transmission geometry at normal incidence. Such a coherent response can only be obtained when a tilt of the sample plane with respect to the normal incidence is introduced due to the emergence of the nonlinearity contribution due to the interface between the gold nanocylinders and the substrate [1].

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# Acoustic Vibrations of Nanoparticles: Mass Sensing and Interface Characterisation

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The investigation of metallic nanoparticles acoustic vibrations is at the interface between plasmonics, nano-thermics and nano-acoustics and can reveal crucial information at the nanoscale. Time-resolved optical measurements of these vibrations (1GHz-1THz) are possible taking advantage the high sensitivity of the surface plasmon resonance to shape and volume variations of the nanoobject [1]. In this kind of experiment, a first femtosecond laser pulse excites the nanoparticle: the energy is absorbed by the electron gas and redistributed to phonons and then the particle environment. During this relaxation process, acoustic vibrations are launched and modulate the optical response of the particles [1]. A second pulse, delayed, monitors the absorption variations that are due to the surface plasmon modulations induced by acoustic vibrations. We will present two sets of results using this technique to get information at the nanoscale on the particles and their environment.

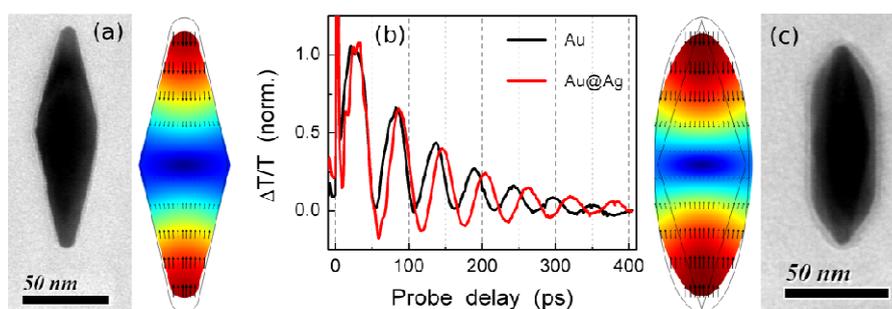


Figure 1. (a-c) TEM images of core gold and core-shell gold-silver particles and illustration of the displacement field of the fundamental vibration mode using finite element analysis. (b) Transient absorption signal showing acoustic vibrations of core and core-shell particles.

The first one is a demonstration of the great sensitivity of gold bipyramid vibrations to a tiny silver deposition (cf. Figure). Investigation of the periods and amplitudes of the observed modes allowed us to estimate the sensitivity limit at 40 attograms of silver per particle [2]. These results show that the use of gold nanoparticles is an interesting path to develop nano-balances since they can perform a multi-criterion analysis (periods, amplitudes, several modes) rather than classical methods based on a single frequency monitoring.

The second one deals with results obtained on core-shell particles (gold-silica and silver-silica) and shows that acoustic vibration measurements permit the characterisation of the nature of the mechanical contact at the interface between core and shell; this information of major importance is non reachable with electronic microscopy imaging [3].

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# Enlightening the acoustic vibrations of single crystalline gold nanorods by very low-frequency Raman scattering

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Gold nanorods (AuNRs) have attracted wide interest in the last decade due to their potential application in many fields. Most of these applications hinge on the shape-dependence of their optical and electronic properties. Besides, crystallinity is likely to play a key role for tailoring properties and functionalities of metal nanoobjects [1].

Single crystalline AuNRs were synthesized using the method described in ref [2]. This procedure includes some modification of the classical seed-mediated method. Using hydroquinone as the reducing agent allowed to synthesize AuNRs with high aspect ratio without appreciable amount of other shapes (see Figure 1a). By varying the synthesis parameters such as the concentration of hydroquinone, seed particles, gold ions and silver nitrate, the AuNRs size and aspect ratio was controlled. The typical dimensions of the AuNRs are of several tens of nanometers in length and their average diameter does not exceed about 8 nm.

This work deals with the study by very low-frequency Raman scattering of the acoustic vibrations of AuNRs. The vibrational frequency is sensitive to either the length or to the diameter of the nanorods depending on the nature of the mode. The narrow AuNRs size distribution results therefore in a low dispersion of frequency for each vibrational mode. As a benefit from this low frequency dispersion, the Raman spectra presented in Figure 1b exhibit several narrow bands in the 20-150 GHz frequency range. Calculations were carried out using a homogeneous continuum model taking into account the elastic anisotropy of gold [3] to get a more accurate picture of the studied nanorods. Thanks to the comparison of the measured and calculated frequencies the different bands observed in the Raman spectra are assigned. These results evidence the sensitivity of the low-frequency Raman spectra on the dimensions (length and diameter) and inner crystalline structure of the nanorods.

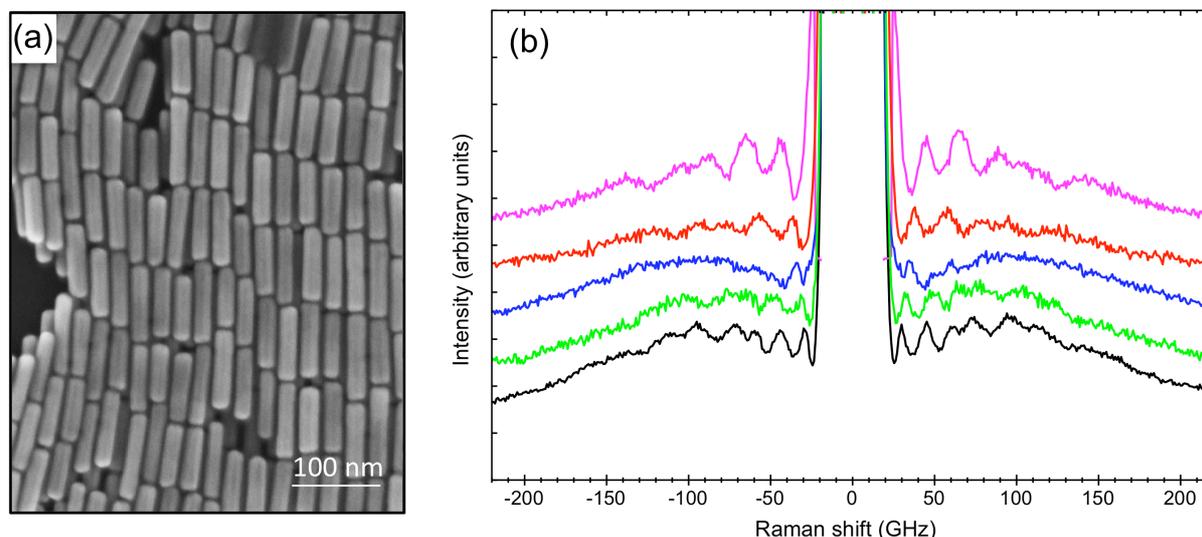


Figure 1. (a) High-resolution SEM-FEG image of gold nanorods. (b) Anti-Stokes and Stokes low-frequency Raman spectra of gold nanorods differing by their sizes and aspect ratios. The spectra are recorded using an excitation source at 647.1 nm. The spectra are vertically shifted for clarity.

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# Photothermal Properties of Gold Nanorods: LeChatelier in Action

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Gold nanorods have tunable plasmonic peaks throughout the visible and near-infrared portions of the electromagnetic spectrum; plasmon band position depends on the aspect (length/width) ratio of the nanorods (see Figure 1).<sup>1</sup>

It is well-known that upon resonant illumination, gold nanorods can generate heat, and this photogenerated heat has been employed as a means to both destroy pathogenic cells and to trigger molecular (usually drug) release.<sup>1</sup>

The notion of molecular release, however, only works if the fundamental thermodynamics of molecular binding to gold nanorods is exothermic; then, an increase in temperature will lead to molecular release in accord with LeChatelier's principle.<sup>2</sup> For endothermic interactions, LeChatelier's principle predicts additional molecular adsorption, rather than desorption, to the gold nanorods. Data that supports LeChatelier's principle will be presented.

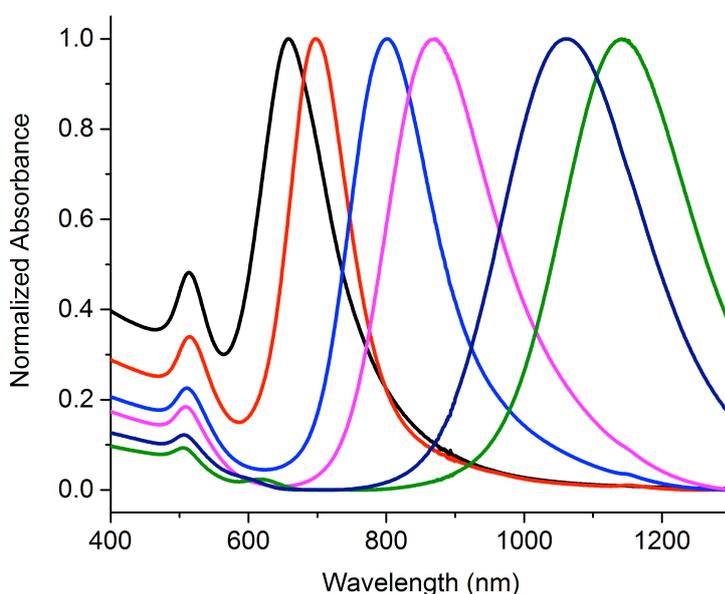


Figure 1. The extinction spectra of gold nanorods from aspect ratio 2 (black) through 7 (green).

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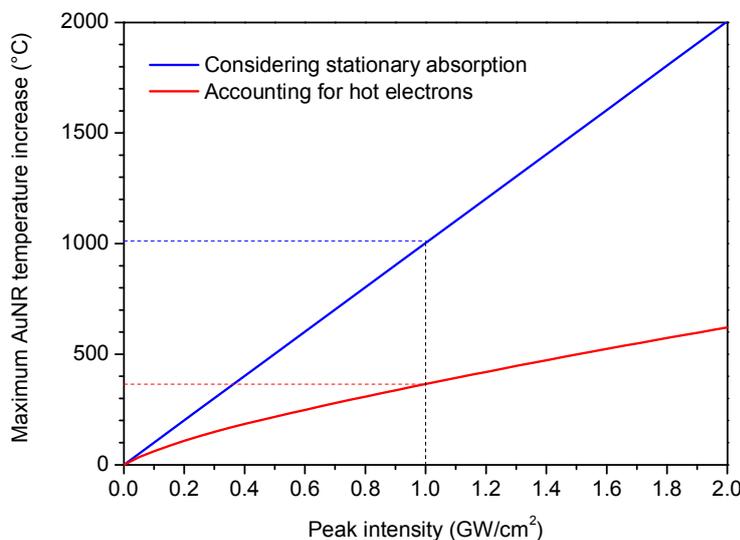
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# Absorption of light by gold nanoparticles under ultrashort laser pulses: not necessarily what you might think

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Exciting plasmonic nanoparticles by subpicosecond laser pulses can generate a lot of interesting phenomena, which can be further exploited in chemical or biomedical applications: localized overheating<sup>1-3</sup>, photoluminescence<sup>4</sup>, electron emission, production of free radicals in water<sup>5</sup>, cavitation<sup>6</sup>. In order to quantitatively analyze and optimize these effects, proper evaluation of the light pulse power absorbed by the nanoparticles is highly required. However, in the literature the only stationary properties are considered for that purpose. In this communication, we show that this may be invalid owing to the optical nonlinearity associated with the photo-generated hot electron distribution. We demonstrate through a simple optical transmission experiment the influence of hot electrons on the absorption cross section of gold nanorods, excited by subpicosecond laser pulses tuned to the longitudinal plasmon resonance spectral domain. The partial melting threshold of the nanorods is reached for a peak intensity of 5 GW/cm<sup>2</sup>, corresponding to a volume density of energy of 2.2 aJ/nm<sup>3</sup>. Below this threshold, the experimental results are interpreted through a model which accounts for the nonthermal nature of the electron distribution and the possible multiphoton excitation<sup>7</sup>. The variation of the effective optical absorption cross-section,  $\langle\sigma_{abs}\rangle$ , with laser peak intensity reveals a strong and complex nonlinearity, which in addition depends on laser wavelength and nanoparticle shape,  $\langle\sigma_{abs}\rangle$  being either larger or smaller than the stationary cross-section value. Besides, we show that for a given pulse energy, the shorter the pulse duration, the greater this deviation from the stationary value. Finally, we illustrate the concrete implications of this discrepancy through the evaluation of the nanoparticle temperature reached after photothermal conversion (see Figure).



*Figure. Maximum temperature increase in gold nanorods (aspect ratio = 4) induced by photothermal conversion of 100-fs laser pulses tuned to the longitudinal plasmon mode, as a function of the pulse peak intensity. Blue: Evaluation by considering the stationary value of the absorption cross section. Red: Calculation accounting for the ultrafast transient evolution of the electron distribution during the pulse passage. At 1 GW/cm<sup>2</sup> the temperature increase reaches only ~1/3 (365 °C) of what is predicted with the usual basic assumptions of the literature<sup>1-3</sup> (1002 °C).*

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# Spatially and temporally reconfigurable temperature control at the microscale.

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We propose and demonstrate a dynamic microscale temperature-shaping technique by tailoring the illumination of a homogeneously distributed gold nanoparticles (NPs) array. The method consists in (i) calculating the heat source density able to create a desired temperature map [1], (ii) using a wavefront engineering technique to reproduce this heat source density in the NPs plane. We validate the method by imaging temperature with wavefront-sensing-based thermal microscopy [2,3].

We experimentally demonstrate the optical projection of multiple tailored temperature patterns with different temperature values at the micrometer scale. Using cultured hippocampal neuron cell images, we also show that this concept is well adapted to the selective and accurate heating of single cells or cellular bodies.

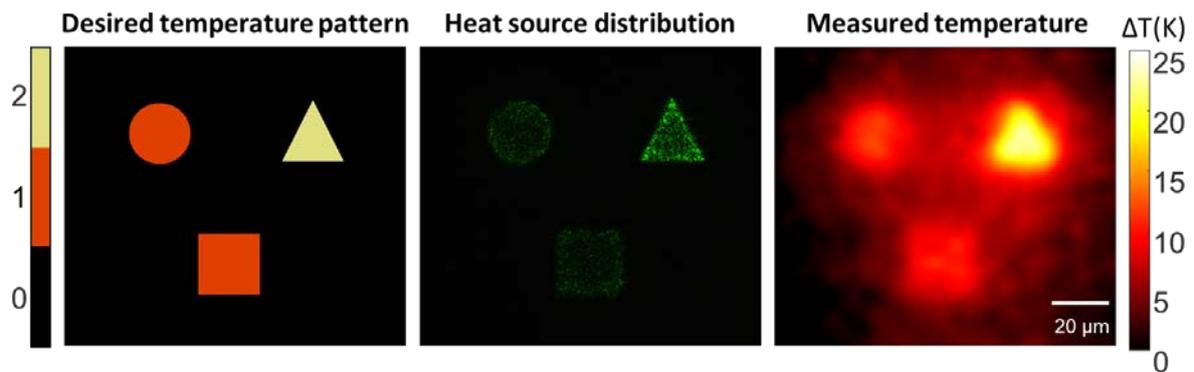


Figure 1. Dynamic temperature shaping at the micrometer scale by exploiting plasmonic absorption of gold nanoparticles

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# Controlled Assembly of Gold Nanoparticles for Plasmonic Based Photothermal Therapy

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Gold nanoparticles (AuNPs) can behave as nanosources of heat under illumination with light at a frequency close to the frequency of the surface plasmon oscillation. In the field of medicine, AuNPs are already commercialized,<sup>[1]</sup> as nanosources of heat, for applications such as photothermal therapy, bio-imaging or drug delivery.

The heating efficiency of AuNPs is determined by: **(1)** the amount of light intensity reaching the NP inside a human body, which is maximized in specific wavelength domains where the attenuation of biological tissue is limited (first domain: [700–950 nm]), and by **(2)** the absorption cross-section which depends on the size ( $\sigma_{Abs} \propto (\text{NP radius})^3$ ), shape and material properties of the NP. Optimizing the heating efficiency by upscaling the size of nanoparticle is not a viable option as they become increasingly inefficient absorbers (the scattering cross section  $\sigma_{Scat} \propto (\text{NP radius})^6$ ). Moreover, from a biological point of view, increasing the nanoparticle diameter is detrimental for nanoparticle biodegradation and elimination from the body due to unfavorable surface/volume ratio.<sup>[2]</sup>

A viable option to solve this problem of optimization would consist to self-assemble small NPs into nanometric clusters.<sup>[3,4]</sup> To our knowledge, few studies were dedicated so far to this option because it remains a challenge to assemble in aqueous solution metal nanoparticles (NPs) into nanometric clusters with a well-defined structure using biocompatible components.

I will present a new strategy for assembling AuNPs into nanometric clusters with various structures based on electrostatic complexation between long polyelectrolyte chains and oppositely charged AuNPs.<sup>[5]</sup> A detailed structural study of the clusters will be first presented based on SAXS and cryo-TEM observations for different diameters of AuNPs ( $D = 4, 13$  and  $40$  nm). In a second part, we will correlate the cluster' structures with UV-Visible spectroscopy and photothermal measurements for the different NP diameters in simple buffer solutions. In a last part, a set of results (structure and photothermal measurements) obtained after NP' internalisation in two types of human fibroblasts (one presenting a lysosomal disorder (cystinosis) and a healthy one) will be presented and compared to reference measurements in simple solutions.

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# High-resolution photothermal microscopy for the detection and characterization of single nano-particles

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Thermal Imaging based on Quadriave Shearing Interferometry (TIQSI) is a non-invasive technique based on the measurement of the thermal-induced refractive index variation of a known medium surrounding a heat source. This photothermal microscopy modality has been developed by G. Baffou in collaboration with Phasics SA<sup>1</sup>. The conventional TIQSI technique enables to map the 2D-temperature distribution induced by illuminated nano-particles under plasmonic resonance with a temperature resolution of 1°C. This technique only requires a conventional white-light optical microscope on which a laser source module must be added along with a SID4 wavefront analyzer.

This SID4 wavefront analyzer provides a phase map and enables to measure the wavefront deformation due to the temperature gradient induced by the heating process. Because the wavefront deformation is tightly related to the refractive index value, it is then possible to calculate the corresponding temperature variation. From the phase map acquisition, a specific algorithm converts the phase signal (i.e. the wavefront deformation) into a 2D-temperature map. Owing to the acquisition speed of the phase signal and to the calculation speed of the temperature, live temperature imaging is performed when temperature variation is inferior to 20°C. If the temperature variation is higher than 20°C, then a non-linear algorithm must be used and the calculation might be longer.

We present in this paper a noise-reduction modality based on synchronous detection enabling to achieve high signal-to-noise ratio measurements. By synchronizing the laser source and the camera acquisition, we are able to average a large number of images without getting affected by the instability of the sample which may introduce noise. We demonstrate the benefit of this new acquisition modality compared to the conventional TIQSI. We achieve a temperature resolution of 92mK.

One of the applications of this thermal imaging system is the detection and characterization of isolated nano-particles. We then applied our system to the characterization of small nano-particles.

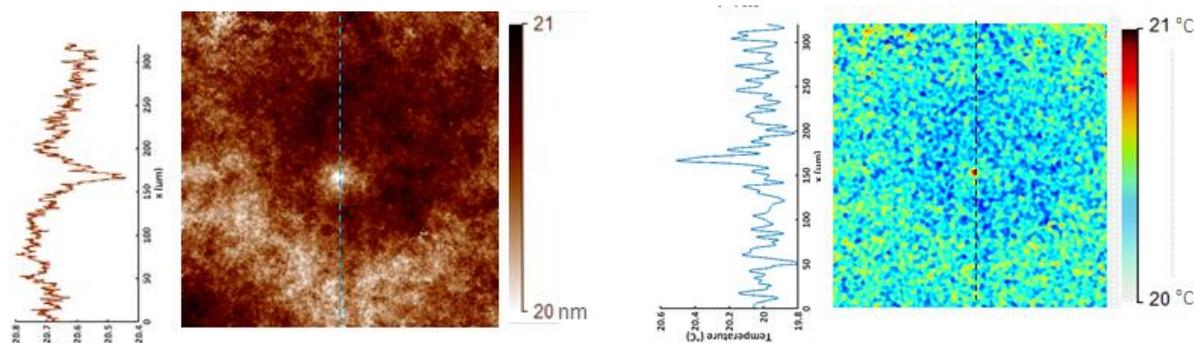


Figure 1. (On the left side) Phase image and phase profile of a 100nm-gold nanobeads imaged with a x20 optical microscope. The phase image is 320 $\mu$ m x 320 $\mu$ m wide. 1000 images have been averaged for a whole acquisition time of 3 minutes. (On the right side) Corresponding temperature map.

We observe that a SNR equal to 5 is obtained on the temperature signal for a temperature variation of 0,5°C.

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# Quantification of heat induced by plasmonic gold nanorods using a $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ luminescent nanothermometer

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$\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}\text{-Bi}^{3+}$  nanoparticles have been demonstrated especially relevant as luminescent nanothermometer because of its very strong temperature dependence of luminescence lifetime of chromium(III) and its high sensitivity on a large temperature range [1]. In order to demonstrate the possibility to use it as local thermal nanoprobe, gold nanorods are synthesized [2] and used as nanoheater. Indeed, under an appropriate excitation such gold nanoparticles may induce a heat due to their plasmonic properties. This anisotropic shape is chosen because of the suitable wavelength excitation in the longitudinal band, which is not absorbed by the nanothermometer (at about 960 nm). The heat generation can be highlighted by thermal camera pictures. The aim of this work is to quantify this local temperature increase. Lifetime measurements were performed in solution but also on powder, and a study on the influence of the distance between nanosensors and nanoheaters and the measured temperature has been carried out by coating the nanosensors with a thickness tunable silica layer. The variation of the optical nanosensor response is promising and should be envisioned to consider this coupled system as a potential candidate for hyperthermia treatment with a precise and controlled temperature.

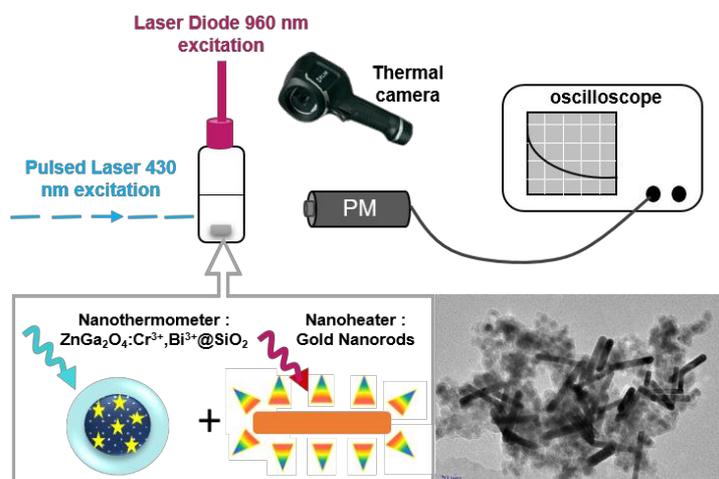


Figure 1. Schematic representation of experimental setup used for local temperature determination induced by plasmonic effect

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# Single-molecule observation of plasmon-assisted Förster resonance energy transfer on DNA-origami

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Plasmonic nanoparticles like gold or silver nanospheres can be exploited for a variety of fields, including for example catalytic<sup>1</sup> or medical<sup>2</sup> applications. In addition, well studied examples consist on the concentration of propagating light and the effect of plasmonic particles on the photophysical properties of single dyes including strong changes in fluorescence lifetime and intensity. The influence of nanoparticles on a two-dye system, which interacts via Förster resonance energy transfer (FRET) with each other, has not been shown yet on the single molecule level. This non radiative energy transfer occurs in a range under 10 nm between a donor and an acceptor dye. To align both of these methods at the nanometer scale the DNA-origami technique<sup>3</sup> can be used as a breadboard (see Figure 1). Previous works showed that this technique can be combined with spherical nanoparticle to show enhancement of dyes<sup>5,4</sup> or FRET<sup>6</sup>.

In this contribution the influence of single spherical gold and silver nanoparticles with different sizes, on the FRET mechanism is determined. Measurements are performed at the single-molecule level on surface immobilized samples. Compared to previous ensemble measurements<sup>7</sup>, which are performed in solution, this approach allows the direct determination of the plasmonic assisted Förster resonance energy transfer efficiency and rate.

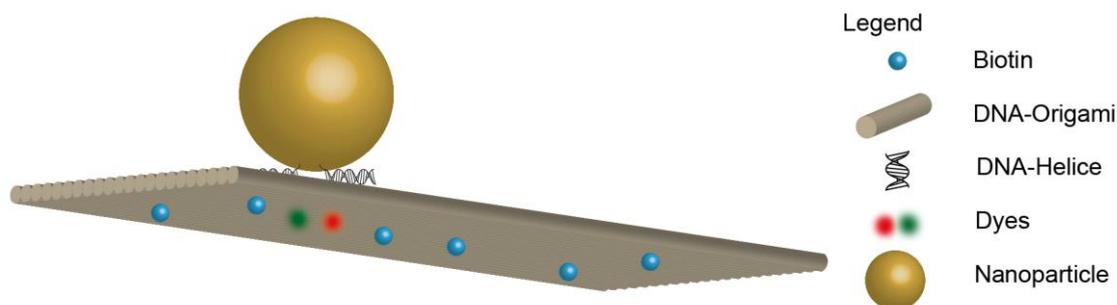


Figure 1: Schematic representation of the employed DNA-Origami.

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# Plasmonic enhancement of single molecule fluorescence using DNA-templated gold nanoparticle dimers

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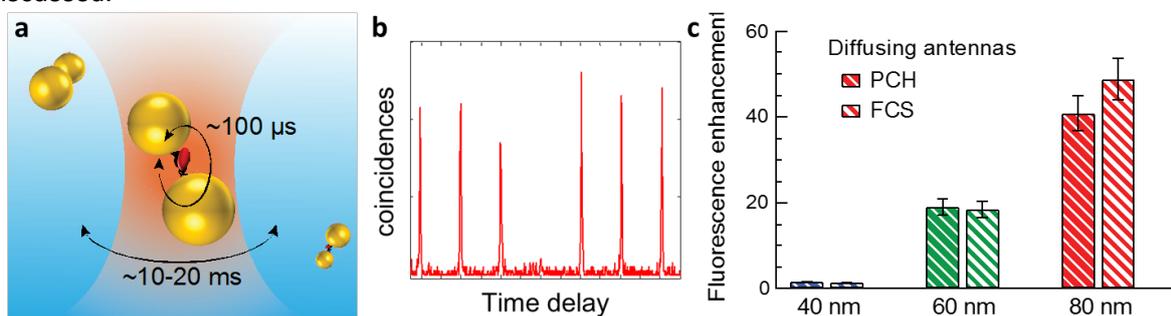
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By providing intense optical fields that are confined at the nanoscale, gold nanoantennas can enhance both the excitation and decay rates of fluorescent emitters by several orders of magnitude. In order to couple efficiently and reproducibly quantum emitters to plasmonic antennas, DNA self-assembly is a particularly flexible and robust technique to introduce a single fluorescent molecule in the gap between gold particles with nanoscale precision (see Figure 1-a).

Single molecule spectroscopy techniques have allowed us to demonstrate that DNA-templated gold particle dimers can enhance the spontaneous emission rates of dye molecules by more than two orders of magnitude, while maintaining single photon emission properties (Figure 1-b).<sup>1</sup> However, the efficiency of the emitter-antenna interaction strongly depends on the size of the plasmonic particles. As shown on Figure 1-c, we have demonstrated that DNA-templated 60 and 80 nm diameter gold nanoparticle dimers, featuring one fluorescent molecule, provide single-photon emission with lifetimes that can fall below 10 ps and typical quantum yields in a 45–70% range.<sup>2</sup>

In order to further increase the coupling efficiency between emitters and plasmonic antennas, it is essential to control the orientation of the transition dipole of the fluorescent molecule with respect to the dimer axis. We are currently investigating how the chemical attachment of the dye molecule to the DNA scaffold (base replacement or intercalation) influences the fluorescence lifetime and quantum yield of the coupled system.

The versatility of nucleotide synthesis also allows the introduction of multiple identical or different fluorescent dyes. In particular, the use of two spectrally-matched organic dyes allowed us to investigate the influence of the gold nanoantenna on non-radiative energy transfer processes.<sup>3</sup> Introducing identical emitters also allows us to study many-body interactions in the gap of plasmonic resonators. A further reduction of the fluorescence lifetime below 1 ps, by reducing the dye-antenna distance and by optimizing the dye orientation, should lead to a strong coupling regime as recently discussed.<sup>4</sup>



**Fig.1** (a) DNA-linked gold particle dimers, associated with a single fluorescent molecule, which are freely diffusing in solution. (b) Photon antibunching measurements of a single dye molecule in the gap of nanoparticle dimers. (c) Fluorescence enhancement factors for different particle sizes, estimated in fluorescence correlation spectroscopy.

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# Plasmon-enhanced Single-molecule Enzymology

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Single-molecule fluorescence studies of enzyme kinetics have revealed marked differences in behavior between seemingly identical molecules.<sup>1</sup> However, the low signal-to-noise ratio (SNR) of such experiments complicates quantitation of the heterogeneity, and limits the single-molecule experiments to dilute environments.<sup>2</sup>

We show numerically that plasmonic enhancement by a single gold particle significantly improves the SNR. (Fig.1) The diffusion of a fluorophore generated by the enzyme is simulated using Brownian dynamics, whereas the optical signal is evaluated using electromagnetic simulations of the plasmon enhancement. The plasmon modifies the excitation rate and the decay rates of the fluorophore, resulting in a modified quantum yield and saturation intensity. We find a 100 fold enhancement in SNR compared to confocal excitation, where the enhancement is dependent on the size/shape of the particle, intrinsic quantum yield of the fluorescent product, and other experimental conditions such as excitation intensity and signal binning.

Currently experiments are conducted for enzymes (alkaline phosphatase) conjugated to single gold particles. The improved SNR will enable the study of single molecules with high SNR in realistic but concentrated biological samples.<sup>3</sup>

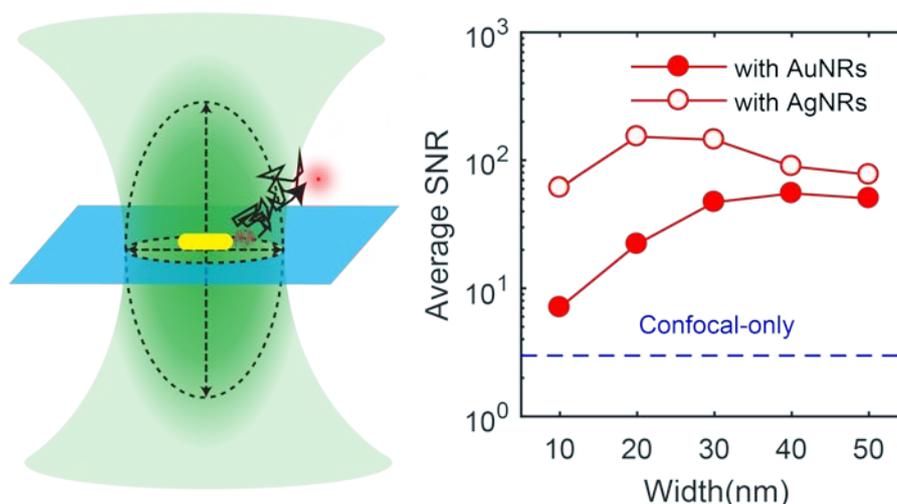


Figure 1. (Left) A proposed scheme: confocal excitation of an enzyme-gold nanoparticle complex. (Right) Average SNR of single enzyme turnovers as a function of particle widths. The simulation is performed with single-enzyme-conjugated gold nanorods of varying widths and identical plasmon resonance wavelength.

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# Real-time spectroscopy of moving nanoparticles using holographic tracking

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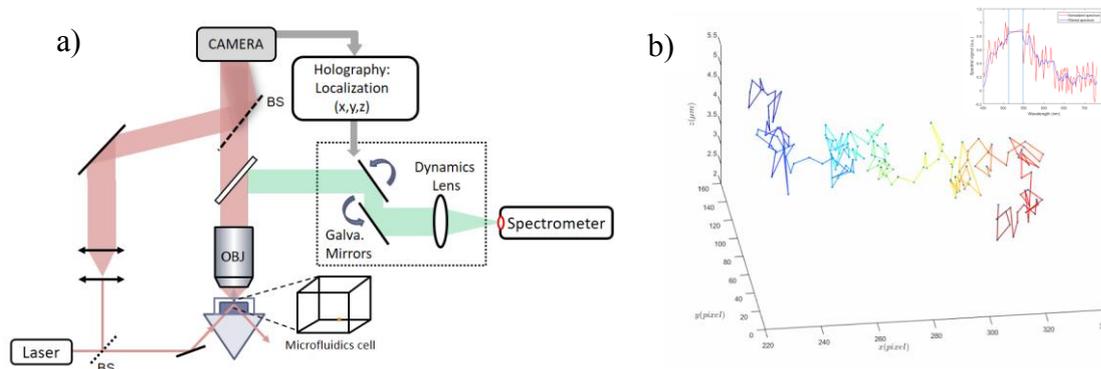
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Because of their high reactivity, metal NanoParticles (NPs) provide various promising applications such as catalysis, cancer treatment,... Many of their properties depend on their electrochemical behavior. At the macroscopic scale, nanoparticle properties are the average of many individual NPs, which can actually differ strongly. Studying electrochemistry at the single particle scale is therefore crucial, as well as challenging.

Since the beginning of 21<sup>st</sup> century, by reducing the electrode size, electrochemists managed to observe an electron transfer between a single NP and an electrode<sup>1</sup>. However, this electrochemical signal does not provide sufficient information about the physical behavior of NP. Using **digital holographic microscopy (DHM)**, we are now able to reconstruct the electromagnetic field scattered by single nano-objects. From this reconstruction, NPs can be localized in real time with sub-diffraction precision (up to  $3 \times 3 \times 10 \text{ nm}^3$  if the SNR = 70). With this optical observation, we can now correlate two signals : electrical current and the position of NP during the experiment which reveals the behavior of a single NP<sup>2,3</sup>.

Besides, the spectral information of NPs in an electrochemical reaction is also required in the local chemical analysis. Unfortunately, spectral studies of single NP *in situ* are extremely difficult due to their Brownian motion. We have developed an **3D spectro-electrochemistry nanoscope** which adds spectral observation to an electrochemical reaction. Using a confocal system in front of the spectroscope, only one NP is studied. In order to compensate the movement of NPs, the localization by DHM is used to drive an adaptive optical system and redirect the light scattered by the NP under study towards the spectroscope (*Figure 1*). We can now track a single gold NP in real time, with a 20 Hz rate, and measure its spectrum. As a result, the interaction between a single NP and its environment can be detected *in situ* by the spectral shift. This new approach should find applications in many fields beyond electrochemistry, whenever the spectrum of the nanoparticle brings additional information. In this contribution, we will present the optical system as well as trajectory tracking and spectral measurements on single gold NPs in water and ionic liquids.



**Figure 1. a)** Experimental setup of 3D spectro-electrochemistry nanoscope. The localisation is used to drive galvanometric mirrors and dynamics lens (variable focal length).  
**b)** Tracking of a single NP and its spectrum (small image)

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# Tuning scattering labels for high-fidelity tracking of fast biological events

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The study of the real-time function of biological structures has attracted a great deal of attention in the last years. In that respect, tracking single-protein behavior by means of fluorescent labels and localization microscopy has been established as the method of choice improving our understanding of life at the single-molecule level. However, the accuracy and speed of fluorescent-based experiments are fundamentally limited by complex photo-physics, saturation and photobleaching.[1]

Interferometric scattering microscopy (iSCAT), relies on scattering labels such as gold nanoparticles (GNPs). The potential of tracking biophysical processes via its scattering signal including sub-protein-sized labels and unlabeled proteins [2] have already reached temporal or spatial resolution in the order of 1 microsecond and 1 nanometer, respectively [3].

However, introduction of a new landscape for single-protein tracking abilities opens new challenges on the design of protein-label constructs suitable for high-speed and high-fidelity trajectories. In order to track fast biological events the diffusivity of scattering labels needs to be sufficient to follow the motion under research. Additionally the diffusion of the scattering label within its anchor potential may not average out at microsecond timescales and therefore the trajectory is found biased by the diffusive motion of the scattering label. Finally, the balance between the acquisition speed and consequent demand on illumination light intensity needs to be accounted for with respect to the particle size and possible particle heating.

In this paper, we take every aspect of protein labeling for high-speed iSCAT tracking into account and distill a set of rules enabling microsecond-resolved trajectories of single-protein motion with a nanometer fidelity. We present theoretical and experimental studies of the particle size dependence as well as the length of the linker between the label and particular structural domain of a protein. The applicability of the concept is demonstrated by tracking the movement of microtubule-associated proteins, such as Ase1.

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