Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information

Surface-Enhanced Spectroscopy on Plasmonic Oligomers Assembled by AFM Nanoxerography

Pierre Moutet[1], Neralagatta M. Sangeetha[1], Laurence Ressier[1], Noélia Vilar-Vidal[2], Miguel Comesaña[2], Serge Ravaine[2], Renaud A. L. Vallée[2], Ana Maria Gabudean[3], Simion Astilean[3], Cosmin Farcau[3]

[1] *Université de Toulouse, LPCNO, INSA-CNRS-UPS, 135 Avenue de Rangueil, Toulouse, 31077, France*

[2] *CNRS, University of Bordeaux, CRPP, UPR8641, 115 avenue Schweitzer, 33600 Pessac, France*

[3] *Institute for Interdisciplinary Research in Bio-Nano-Sciences, Babes-Bolyai University, Cluj-Napoca, Romania*

I. Characterization of the synthesized colloidal nanoparticles

A summary of the characterizations of the Au@TDSP nanoparticles synthesized for SERS experiments is given in Figure SI-1. The size histogram presented on Figure SI-1a, constructed from Transmission Electron Microscopy (TEM) images (as the one shown in the inset) gives a mean value of 102 ± 7 nm for the diameter of the nanoparticles. The optical extinction spectrum presents a well-defined band with the maximum at 540 nm, specific for spherical gold nanoparticles of such sizes.

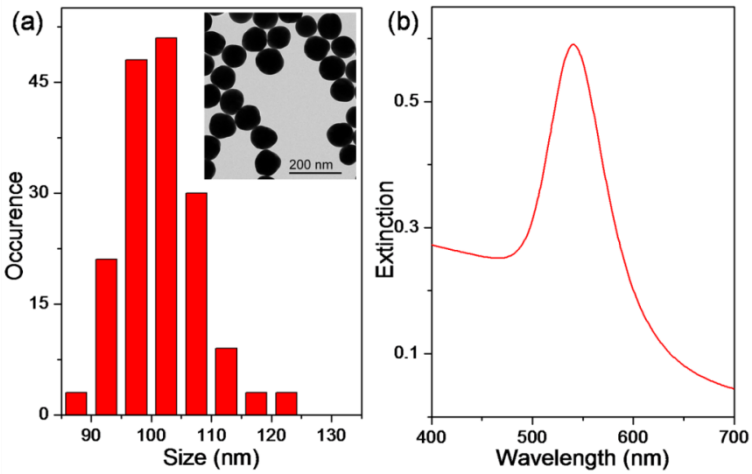

Figure SI-1. (a) Size histogram with typical TEM image and (b) optical extinction spectrum of 100 nm Au@TDSP nanoparticles.

Au@SiO_2 spherical core-shell particles were synthesized prior to grafting Rhodamine B on their surface. Figure SI-2 presents the morphology, the size distribution and UV-vis extinction of the Au core and theAu@SiO_2 core-shell nanoparticles.

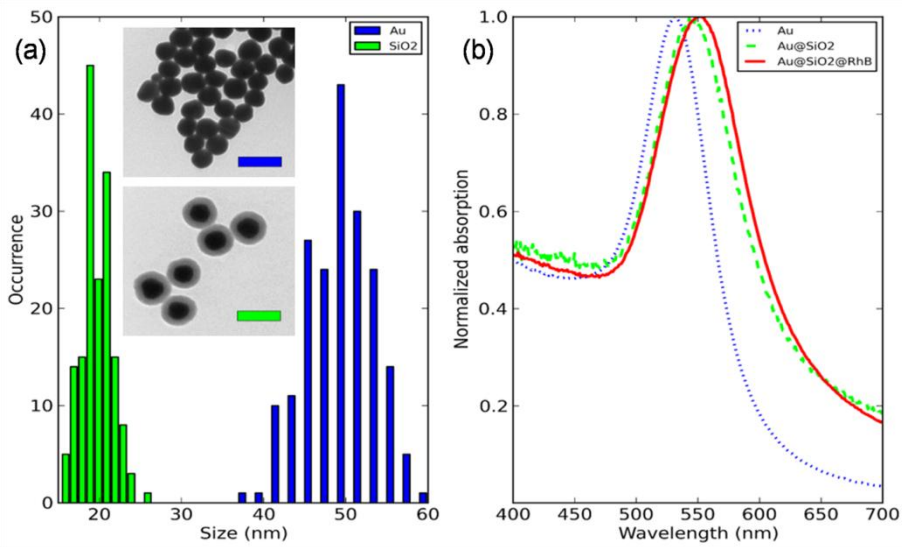

Figure SI-2. (a) Size histogram with typical TEM images for the Au core and SiO_2 shell, and (b) optical extinction spectra of 90 nm Au@SiO_2 nanoparticles, at different stages.

The insets of Figure SI-2a exhibit TEM images at the first (Au) and second stages (Au@SiO_2) of the synthesis. On the basis of several such recorded images, histograms of the sizes of the core and shell were drawn. The histograms give a mean value of the core diameter of 50 ± 5 nm and a shell thickness of 20 ± 2 nm. Figure SI-2b further exemplifies the good quality of the synthesized ensemble of particles with narrow UV-visible absorption spectra around the plasmon resonance frequency, corresponding to such shapes and sizes of the particles [K. L. Kelly*et al.*, J. Phys. Chem. B 2003, 107, 668; K. A. Willets*et al.*, Annu. Rev. Phys. Chem. 2007, 58, 267]. The long wavelength shift observed at different synthesis stages is explained by the large sensitivity of plasmon resonances to an increase of the refractive index, in the immediate surrounding of the particles. Indeed, the gold cores are surrounded by a silica shell of high refractive index (n = 1.45) and the subsequent layer of highly polarizable Rhodamine B molecules grafted on the outer silica shell surface further increases the local refractive index.

II. FDTD calculations

FDTD calculations of the photonic (total) local density of states (LDOS), the far-field radiated power ($P_l^r(\omega)$) and Purcell factors (F) were performed. According to ref. [A. Taflove *et al.*, Advances in FDTD Computational Electrodynamics: Photonics and Nanotechnology; Artech House, 2013], the LDOS in the direction $l \in$ {x,y,z} is:

$$D_l(x_0,\omega) = \frac{4}{\pi}\epsilon(x_0)P_l(x_0,\omega), \qquad (1)$$

where $P_l(x_0,\omega)$ is the power radiated by an impulsive dipole current source $J = e_l\delta(x-x_0)p(t)$, located at x_0; $\epsilon(x_0)$ is the dielectric constant at this point and e_l is the unit vector in the direction *l*. $P_l^r(\omega)$ is obtained by using the same source but collecting the power in the far-field, far (in terms of the incident wavelength) from the considered oligomeric structure. In the FDTD model here employed, accumulating the Fourier transform $\hat{E}_l(x_0,\omega)$ of the field generated at x_0 by the impulsive dipole current source yielded the complete LDOS spectrum at x_0:

$$D_l(x_0,\omega) = -\frac{2}{\pi}\epsilon(x_0)\frac{Re[\hat{E}_l(x_0,\omega)\hat{p}(\omega)^*]}{|\hat{p}(\omega)|^2} \qquad (2)$$

and $P_l^r(\omega)$ in the far-field in a single calculation. In each geometry, we computed the LDOS and $P_r(\omega)$ twice, the impulsive dipole current source mimicking the quantum emitter being close to either the specific oligomer structure or the glass substrate taken as a reference. The Purcell factor F is finally obtained by dividing the LDOS of the structure by the LDOS of the

reference:

$$F_l(x_0,\omega) = \frac{D_l^{oligo}(x_0,\omega)}{D_l^{glass}(\omega)} \quad (3)$$

Defined in such a way, the Purcell factor consists in a radiative part, which is related to the signal emitted in the far-field

$$F_l^r(\omega) = \frac{P_l^{r,oligo}(\omega)}{P_l^{glass}(\omega)} \quad (4)$$

and a non-radiative part, which is the part absorbed in the metal by Ohmic losses. By neglecting the enhancement factor originating from the excitation, the fluorescence emission spectrum of the molecule in the oligomer is:[48]

$$S(\omega) = \frac{\gamma_{r0} f_0(\omega) F_l^r(\omega)}{\left[\gamma_{r0}\left[\int_0^\infty f_0(\omega) F_l(x_0,\omega) d\omega\right] + \gamma_{nr\,0}\right] * \eta_0 f_0(\omega_{max})} \quad (5)$$

where γ_{r0}, $\gamma_{nr\,0}$, η_0 and $f_0(\omega)$ are the radiative, non-radiative decay rates, quantum efficiency and integral-normalized fluorescence spectrum of the isolated molecule, respectively. According to the total decay rate $\gamma_0 = \gamma_{r0} + \gamma_{nr\,0} = \frac{1}{2.9} ns^{-1}$ measured for Rhodamine B in ethanol and the reported [C.V. Bindhu *et al.*, J. Phys. D: Appl. Phys. 1996, 29, 1074] value $\eta_0 = \frac{\gamma_{r0}}{\gamma_{r0}+\gamma_{nr\,0}} = 0.82$ of its quantum efficiency in methanol, we could numerically obtain the emission spectra and Purcell factors of chosen oligomers. The decay time of the single emitter is given by $t_F = \frac{2.9}{F_l(x_0,\omega)} ns$.

III. Stability of the SERS signal

One concern in SERS studies on individual few-particle oligomers could be the stability of the SERS signal. To verify the reproducibility of our results we performed additional experiments in the following way: after scanning the chosen oligomer with horizontally polarized excitation, followed by a scan with vertical polarization, we re-scanned the oligomer with the horizontal polarization, to verify if the initial result was recovered. Figure SI-3 presents such a result on the NP trimer discussed in the manuscript on Figure 4. The SERS images and spectra in figure SI-3 are denoted as H' – the first scan with horizontal polarized excitation, V – the scan with vertical polarization, and H'' – the second scan with horizontal polarization. The result was positive, the second horizontal scan being remarkably similar with the first one.

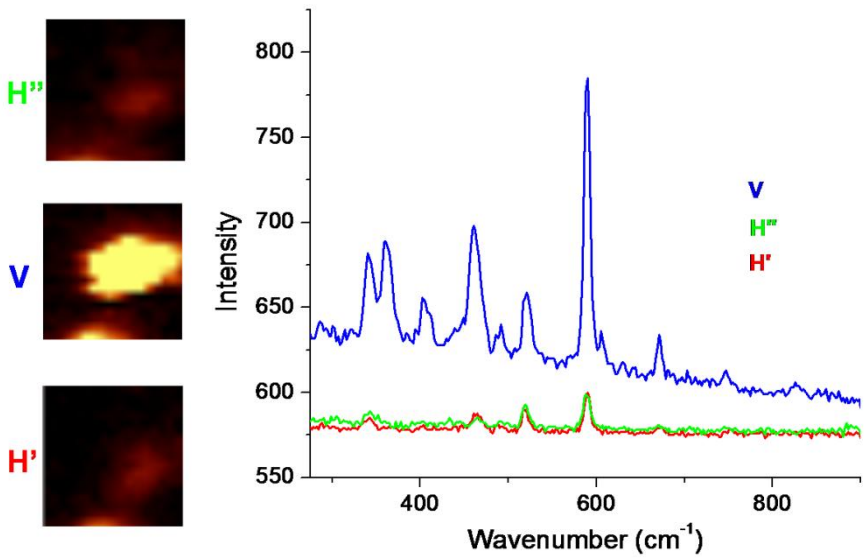

Figure SI-3. SERS images and spectra corresponding to a series of sequentials scans, with the excitation polarized horizontally (H'), then vertically (V), and again horizontally (H'').