Supporting Information

Two-Photon Luminescence of Single Colloidal Gold NanoRods: Revealing the Origin of Plasmon Relaxation in Small Nanocrystals

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This document contains complementary information and figures regarding sample preparation, instrumental setup, and sample characterization.

Sample preparation :

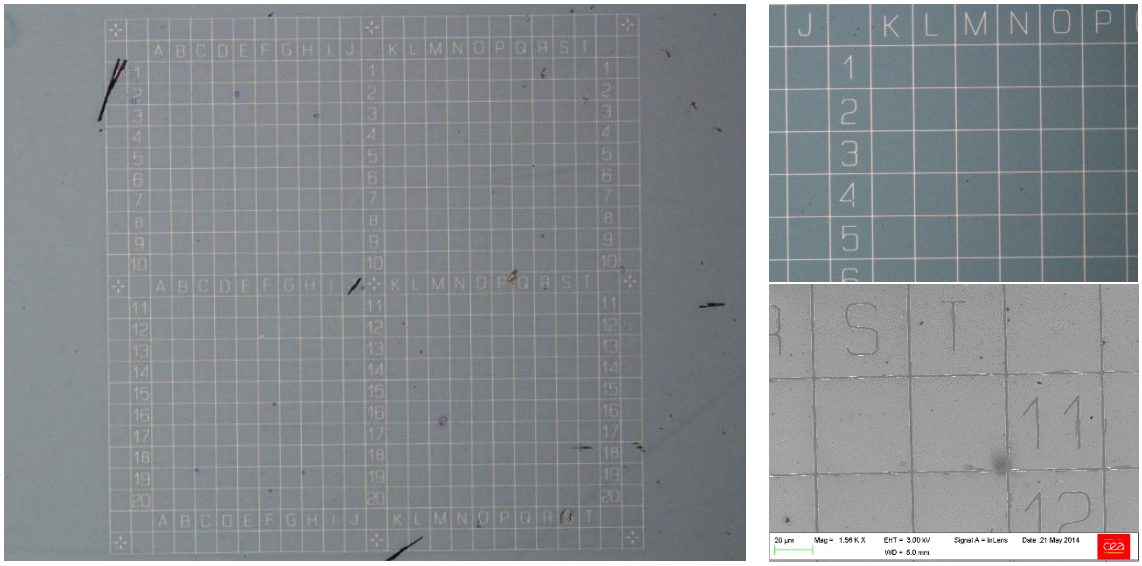

Figure S1 : SEM image of an Indium Tin Oxide (ITO) coated glass cover slide including e-beam lithography fabricated grids with specific landmarks to enable easy localization of the considered nanorods, from SEM characterization to AFM (see figure S2 below) and optical microscopy

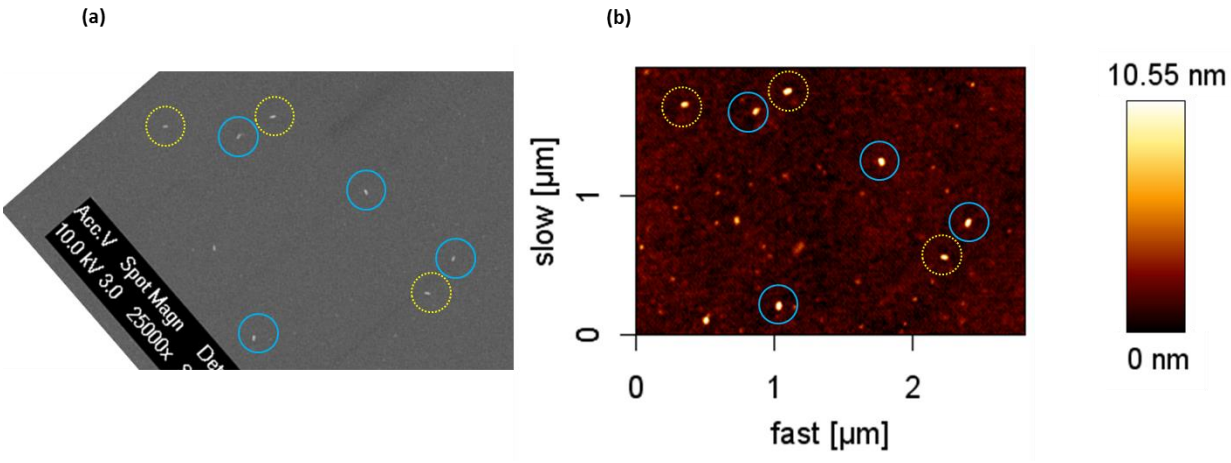

Figure S2 : SEM (a) and AFM (b – see figure 2) characterization of the same area.

Experimental set-up :

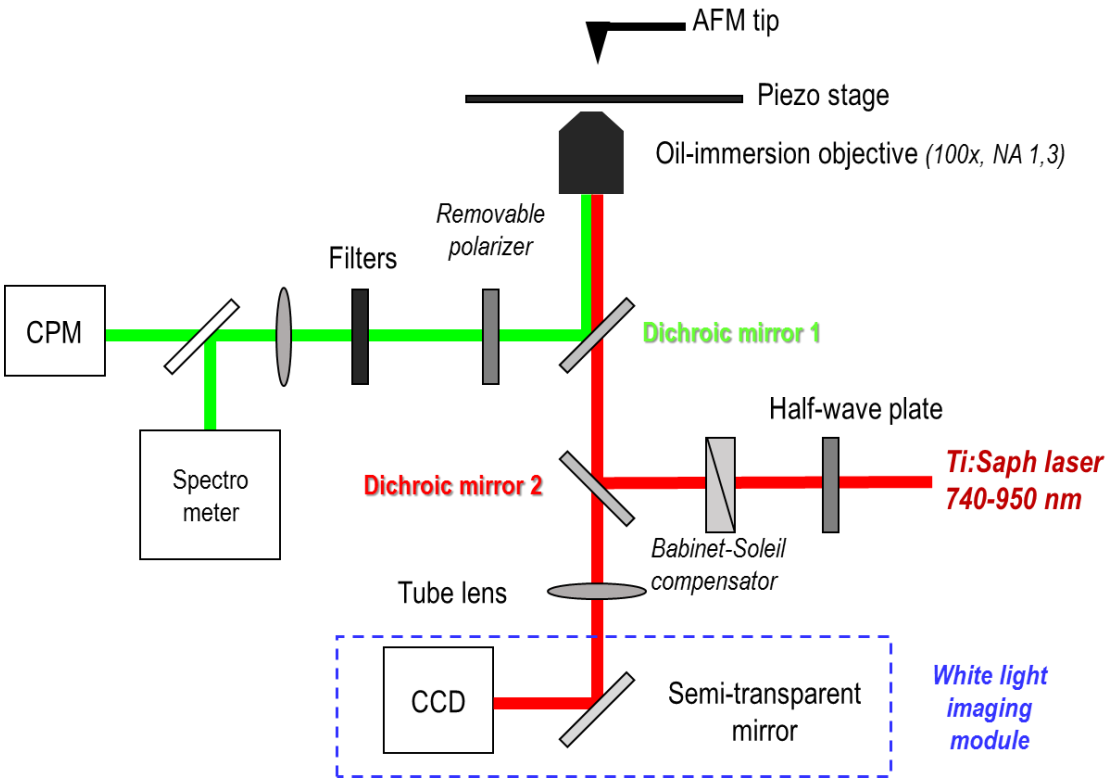

Figure S3 : Combined TPL and AFM microscopy set-up set-up involving an inverted microscope (Olympus IX71) coupled to a cantilever type AFM platform (NanoWizard III, JPK) and associated to a femtosecond Ti-sapphire laser excitation (Tsunami, SpectraPhysics delivering 100 fs pulses with a 80 MHz repetition rate over the spectral range covering 770 to 950 nm). In order to correlate topographic and optical measurements, the requirement for this experiment is the preliminary alignment of the AFM tip with the laser spot at the focus, the sample being then raster scanned enabling simultaneous topography (tapping mode) and TPL recording. The laser beam is linearly polarized (a Babinet-Soleil compensator was adjusted so as to compensate any depolarization effects in the optical path to the sample). Laser polarization together with average power can be controlled using sets of half-wave plates and polarizers. Special attention was taken concerning the choice of the power intensity at the level of the sample since gold nanowires are very sensitive and can easily be melted or burned once subjected to high power intensity. After reflexion onto a dichroic mirror (SemRock FF750-SDi02-25x36), the Ti-Saph excitation beam is focused onto the sample using an oil immersion 100x microscope objective. The emitted TPL is collected through the same microscope objective and separated from the incident light by a dichroic mirror (SemRock FF735-Di670-25x36). The signal is then sent either to a channel plate multiplier working in the photon counting mode (Perkin Elmer MP-993-CL) or to a spectrometer coupled to a CCD camera (Andor DU401-BR-DD) for detailed study of the emission spectra. Excitation spectra were determined from measurements of the whole emitted light using the previously mentioned CPM photomultiplier associated to a set of filters cutting the fundamental beam (SemRock razor edge 785, stopline 785 and 808, FF735 and FF-01-750).

Comparison of the TPL signal of fluorescein molecules dispersed in solution

The TPL signal of one single nanorod was compared to the two-photon fluorescence signal of fluorescein molecules dispersed in a water solution. These molecules are indeed currently used as reference in two-photon absorption measurements [*M. A. Albota, C. Xu, and W. W. Webb. Two-photon fluorescence excitation cross sections of biomolecular probes from 690 to 960 nm, Applied Optics, 1998]*

A droplet of solution was deposited onto an ITO-glass substrate and excited in comparable conditions as for single GNR (λ=800nm, use of the same 100x oil-immersion objective for both excitation of the molecules and signal detection as for GNRs)

The signal for a fluorescein solution with concentration : C = 1,8x10-5mol.L-1 was measured to be about 5000 counts/s for an average **1 mW** excitation.

Considering the Gaussian beam profile of the laser, the excited focal volume is $V \sim 2.\pi w_0^2.z_R$, with w_0 the beam waist (400 nm) and Z_R the Rayleigh $z_R = \pi w_0^2 / \lambda$ (thus V = 0.6 μm^3). This represents about 6000 molecules, thus leading to an average **0.8 counts/s for a single molecule**.

On the other side, the maximum TPL signal measured for a GNR excited with an average 20 μW, is 3000 counts/sec, which can be extrapolated to **7.5 10^6 counts/s**, considering an average 1mW power excitation (excitation conditions of the fluorescein solution, as detailed above), which thus correspond to the signal of about 9 million fluorescein molecules !

In other words, we can conclude that the two-photon brightness of a single gold nanorod is 9. 10^6 higher than the two-photon brightness of a single fluorescein molecule.

Influence of the excitation power :

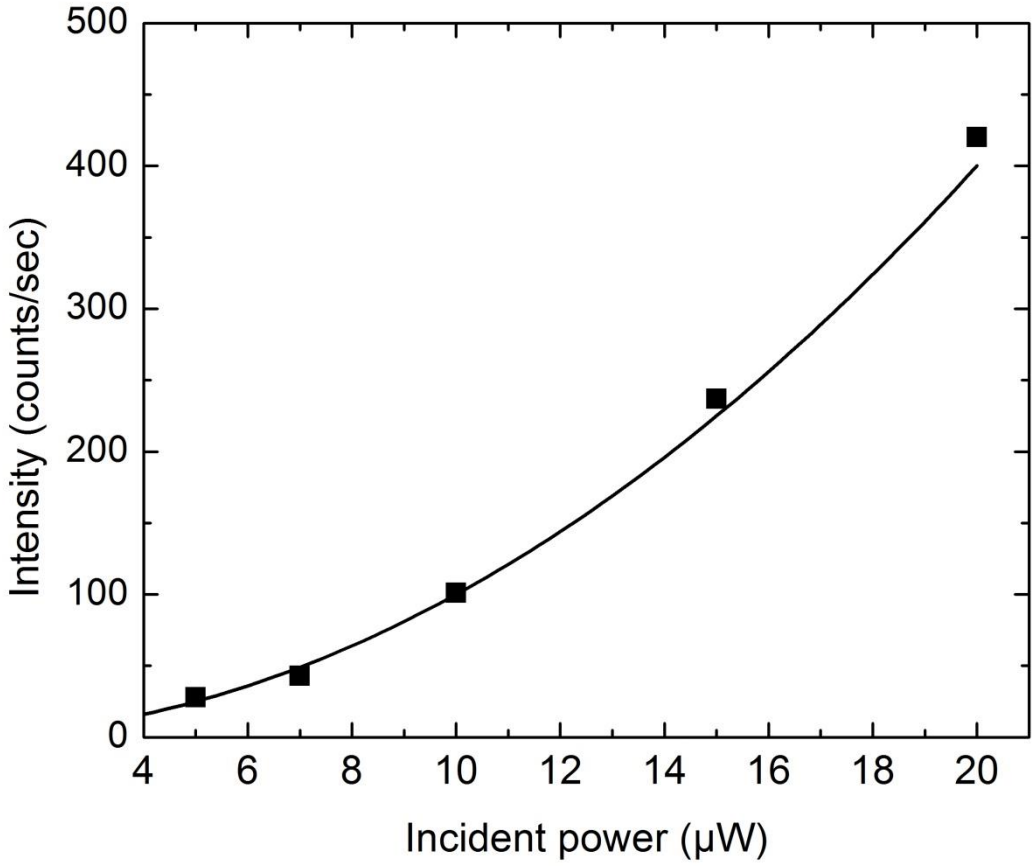

Figure S4 : Dependence of the nanorods luminescence intensity with the exciting beam power. Intensity measurements were achieved using a channel plate multiplier working in the photon counting mode (Perkin Elmer MP-993-CL). Excitation was performed at the nanorods longitudinal resonance with a polarization along the GNR long axis. The continuous line represents a parabolic fit of the experimental data (squares) : $I_{TPL} \alpha I_{\omega}^{2}$

Extinction spectrum:

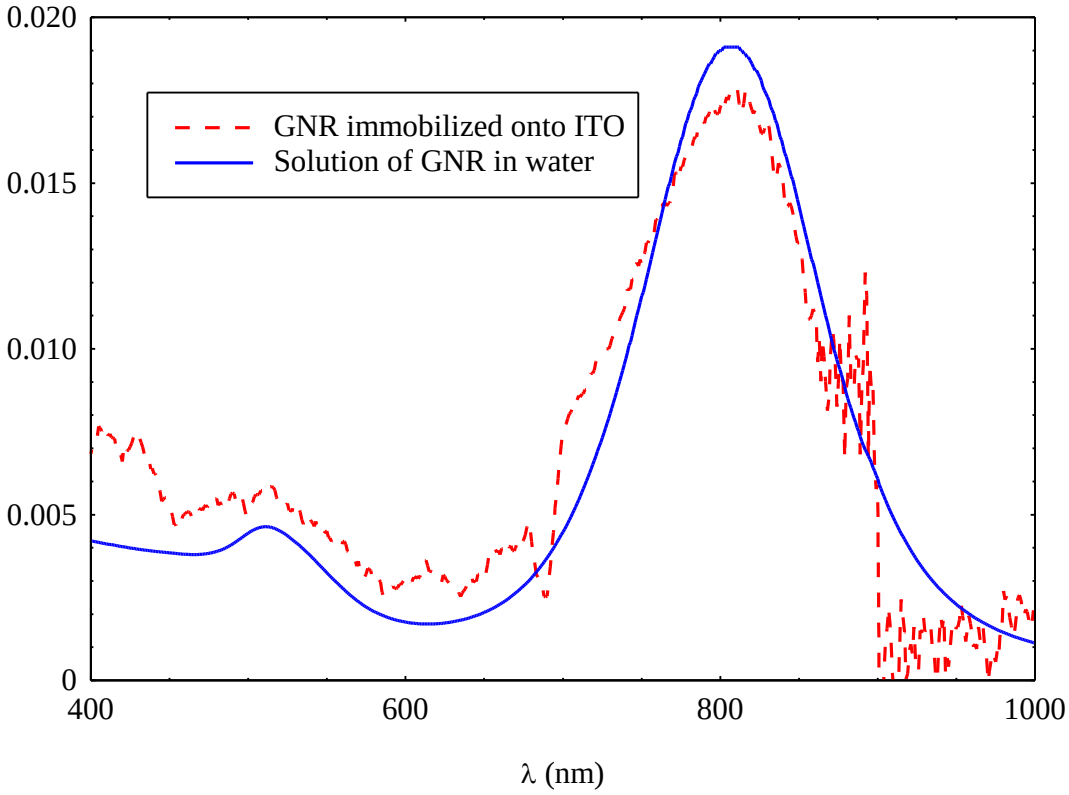

Figure S5 : Extinction spectrum of an ensemble of GNR either dispersed in water (*blue continuous line*) or immobilized onto an ITO glass substrate (*dashed red line*)

Gans-Mie theory :

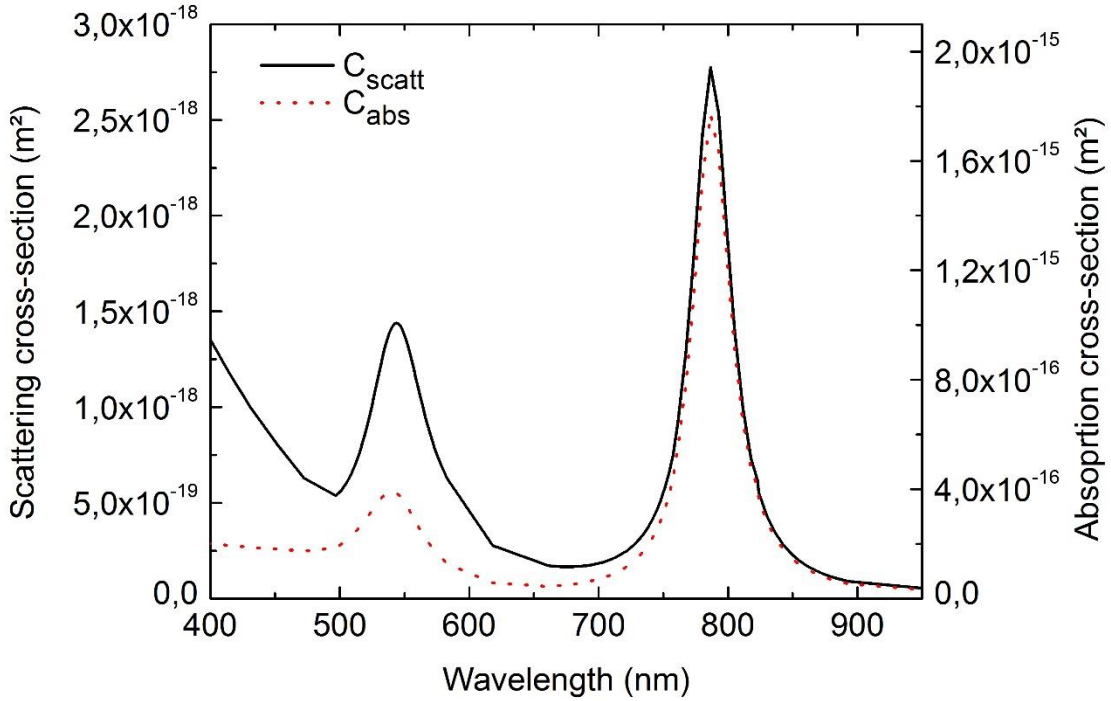

Figure S6 : Calculation of the scattering (C_{sca} – left axis) and absorption (C_{abs} – right axis) cross section of a single 10 nm x 40 nm GNR using the Gans-Mie theory

Influence of the excitation wavelength on the TPL spectrum of a single nanorod

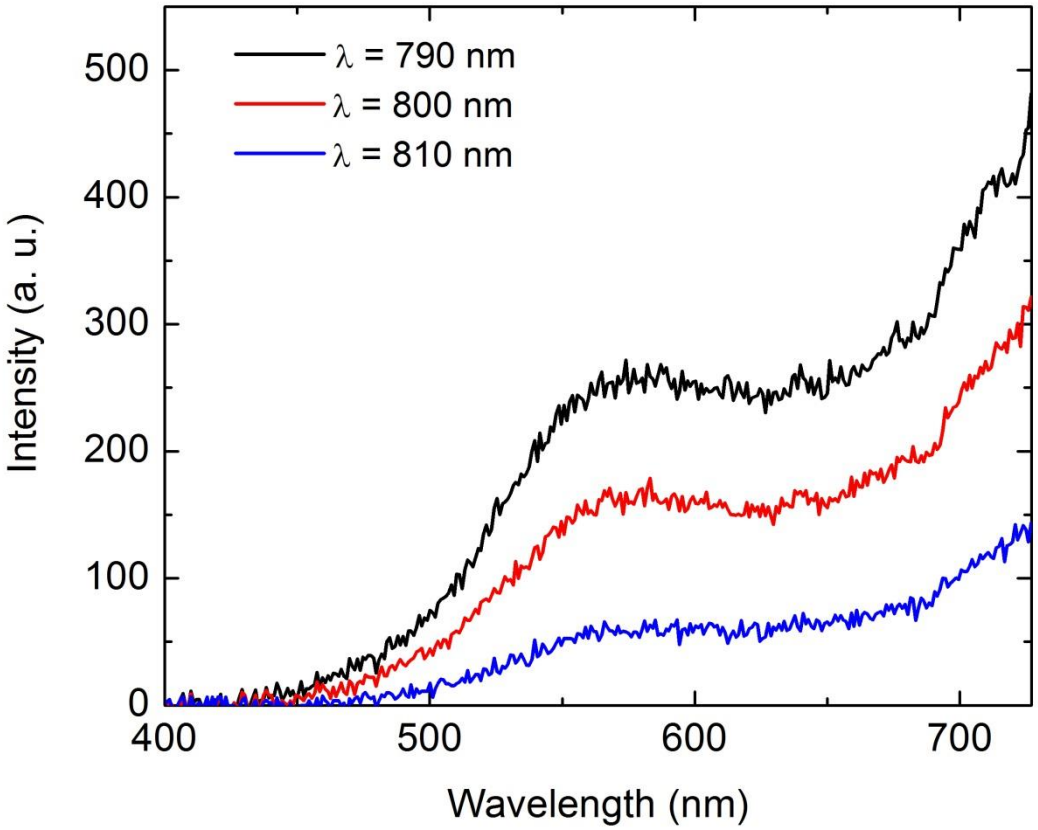

Figure S7 : TPL emission spectra of a single GNR excited along its long axis with different excitation wavelengths, close to the GNR longitudinal resonance, $\lambda_{LSP}{}^{L}$. The excitation power was kept constant (20 µW). The spectra are corrected from the wavelength sensitivity of the CCD camera (Andor DU401-BR-DD).