SPECTRAL PROPERTIES OF THE SURFACE PLASMON RESONANCE AND ELECTRON INJECTION FROM GOLD NANOPARTICLES TO TiO_2 MESOPOROUS FILM: FEMTOSECOND STUDY

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Supplementary information.

SI 1.

The size parameter is given by $x=ka$, a is the radius of the sphere and $k=2\pi/\lambda$ is the wave number, λ the wavelength in the ambient medium, $m=(\varepsilon_1\mu_1)^{1/2}/(\varepsilon\mu)^{1/2}$ is the refractive index with respect to the ambient medium, ε_1 and μ_1 are the permittivity and permeability of the sphere and ε and μ are the permittivity and permeability of the ambient medium.

The efficiencies Q_{ext}, Q_{sca} and Q_{abs} for the interaction of radiation with a sphere of radius a are cross sections σ_{ext}, σ_{sca}, σ_{abs} normalized to the geometrical particle cross section, $\sigma_g=\pi a^2$.

$$Q_{ext} = Q_{sca} + Q_{abs}.$$

$$Q_{ext} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\cdot \mathrm{Re}(a_n + b_n)$$

$$Q_{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2 + |b_n|^2\right)$$

E. C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and Related Plasmonic Effects (Elsevier, Amsterdam, 2009).

SI 2.

The average number of photons per AuNP was estimated from the adsorbed optical energy (according to the laser pulse intensity, the spot size and the sample absorbance) and the concentration of gold nanoparticles. The electronic temperature rise was estimated from the gold heat capacity the adsorbed optical energy per AuNP. However, these values should be taken with care since uncertainties on the spot size are quite large (~30%).

The injected energy is subsequently redistributed among the electrons by electron-electron (e-e) scattering eventually leading to the establishment of an electron temperature T_e, and transferred to the lattice, leading to thermalization of the metal electron gas and lattice T_L. The theory is valid at low excitation power when the rise of the electronic temperature in not higher then ΔT_e~ 1000 K. The change in the electron gas temperature dT_e and increment in the thermal energy δQ from the laser pulse are related by the expression $\delta Q = c_e dT_e$

$$c_e = \frac{\pi^2 k_B^2}{2E_F} T_e \cdot N = g \cdot T_e N$$

$$g = \pi^2 k_B^2 / 2E_F$$

here c_e electron heat capacity, N=1.26 10^5 is a number of free electrons in the particle of 16 nm diameter, E_F = 5.53 eV is Fermi energy of gold, k_B is Boltzmann constant.

By neglecting all kinds of energy dissipation ("sudden approximation") the transient electron temperature is

$$\Delta T_e = \sqrt{\frac{2Q}{gN} + T_L^2} - T_L$$

ΔT_e of 20 K corresponds to the fluence of 24 μJ/cm^2. The low perturbation regime is realized in the present work. c_e being much smaller than the lattice heat capacity C_L, the final temperature rise T_L - T_0 of the fully thermalized electron-lattice system is always much smaller than T_e. It is of order of T_L - T_0 ~$c_e\Delta T_e/C_L$~$0.01\Delta T_e$.

SI 3.

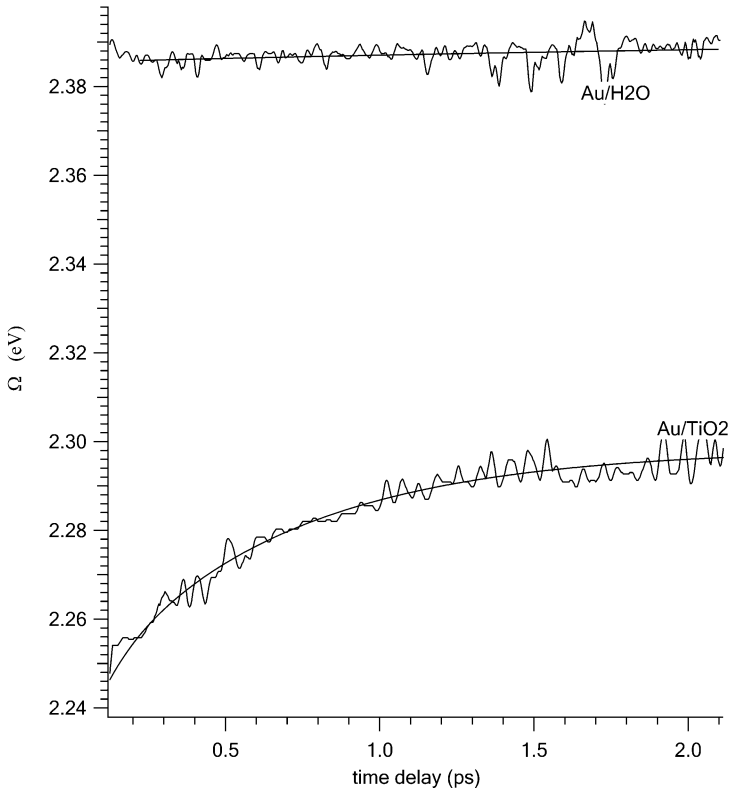


Figure SI3.1 Temporal evolution of the bleaching peak of transient absorption spectra of AuNP in aqueous colloid and in the mesoporous TiO_2 film.

SI 4.

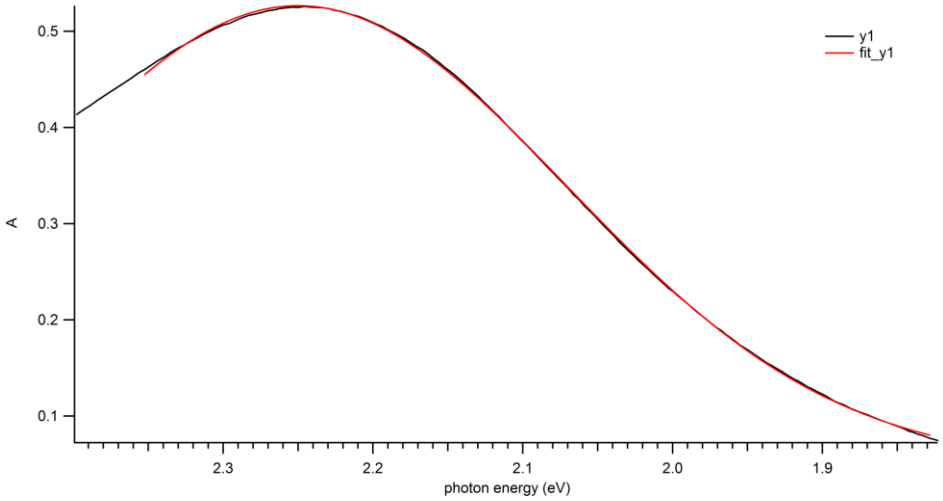
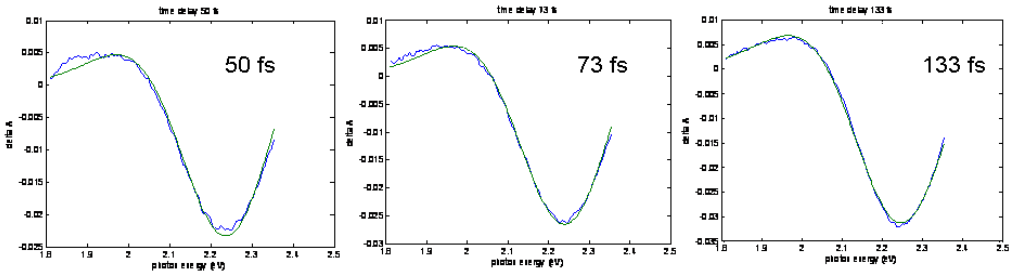


Figure SI4.1. y1 is the spectrum of Au/TiO_2 film. Fit_y1 is the Gauss fit profile of y1:

$A = P_{abs}^{\,0} \Big/ \sqrt{2\pi \cdot w_0^{\,2}} \cdot \exp\left(-\frac{1}{2} \cdot \frac{\left(\omega - \Omega_{SPR}^{0}\right)^2}{w_0^{\,2}} \right)$, where $w_0 = 0.179 \pm 0.0004$ and $\Omega_{SPR}{}^{0} = 2.25 \pm 0.0002$ eV



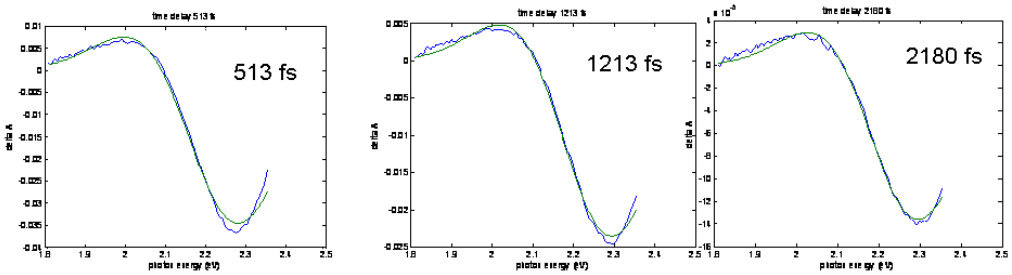


Figure SI 4.2 Examples of fitting of some selected transient spectra by a difference of Gaussian functions $\Delta A(\omega,t) = P_{abs}(t) \Big/ \sqrt{2\pi \cdot w(t)^2} \cdot \exp\left(-\frac{1}{2} \cdot \frac{\left(\omega - \Omega_{SPR}(t)\right)^2}{w(t)^2} \right) - P_{abs}^{\,0} \Big/ \sqrt{2\pi \cdot w_0^{\,2}} \cdot \exp\left(-\frac{1}{2} \cdot \frac{\left(\omega - \Omega_{SPR}^{0}\right)^2}{w_0^{\,2}} \right)$.