Heterogeneity of gold nanorod studied with two-dimensional electronic spectroscopy

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INTRODUCTION

Gold nanorods (AuNRs) have shown great potentials in biological and biomedical application such as molecular imaging, drug delivery, or photothermal therapy.[1] The optical properties of these elongated nanoparticles depend on their shape anisometry. The AuNR-based longitudinal localized surface plasmon resonance (longitudinal LSPR) band is very sensitive to the AuNR's aspect ratio and the surrounding local environment.[2] We investigate for the first time with a pulse-shaper-based two-dimensional electronic spectroscopy (2DES) these noble metal nanoparticles.

[1] Huang XH; Neretina S; El-Sayed MA. Advanced Material S. 2009. 21, 4880-4910.
[2] Link S; Mohamed MB; El-Sayed MA. Journal of Physical Chemistry B. 1999. 103, 3073-3077.

GOLD NANORODS

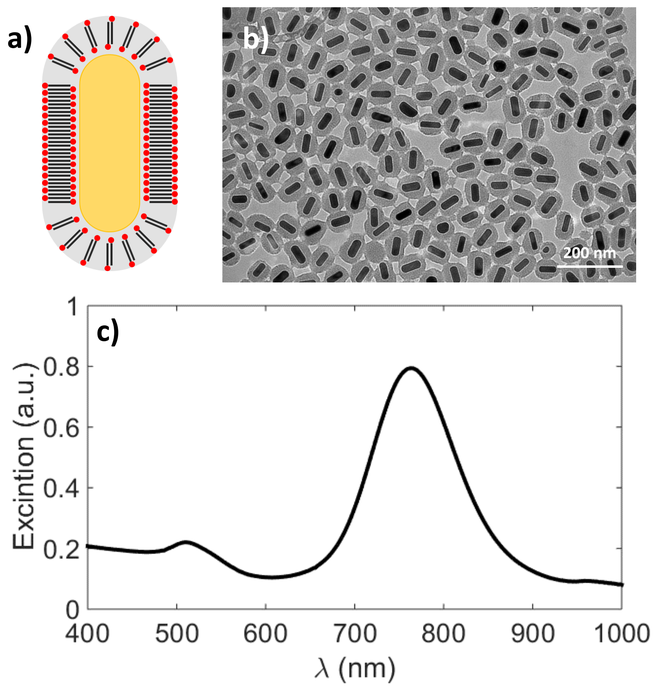
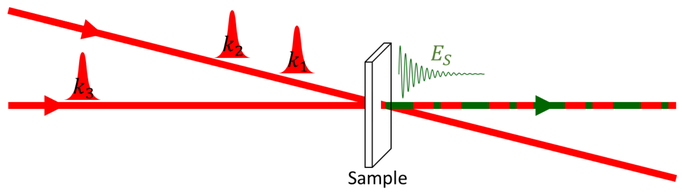


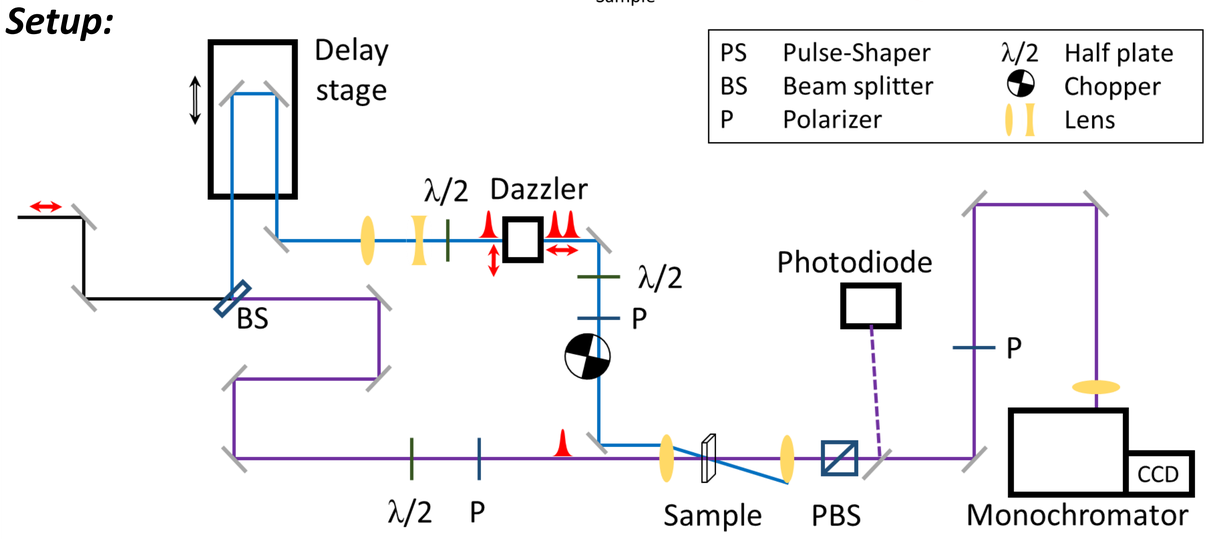
Figure 1: a) Schematic representation of coated AuNR; b) TEM image of AuNRs after silica coating process; c) UV-visible spectra of AuNRs. The absorption band at 510 nm corresponds to the transverse surface plasmon resonance mode, and the absorption band at 760 nm corresponds to the longitudinal mode.

TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

Principle:



Setup:



RESULTS

Differential transmittance spectra:

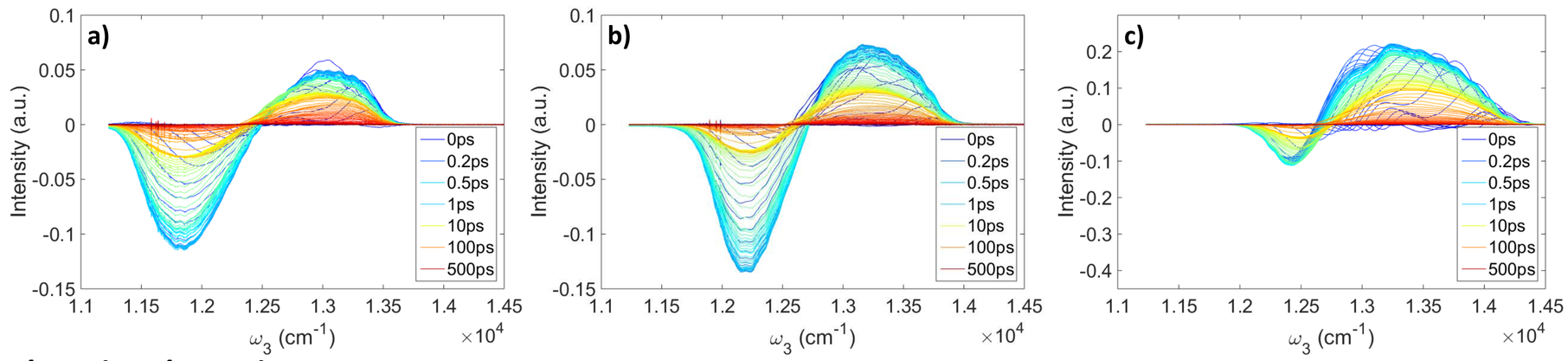
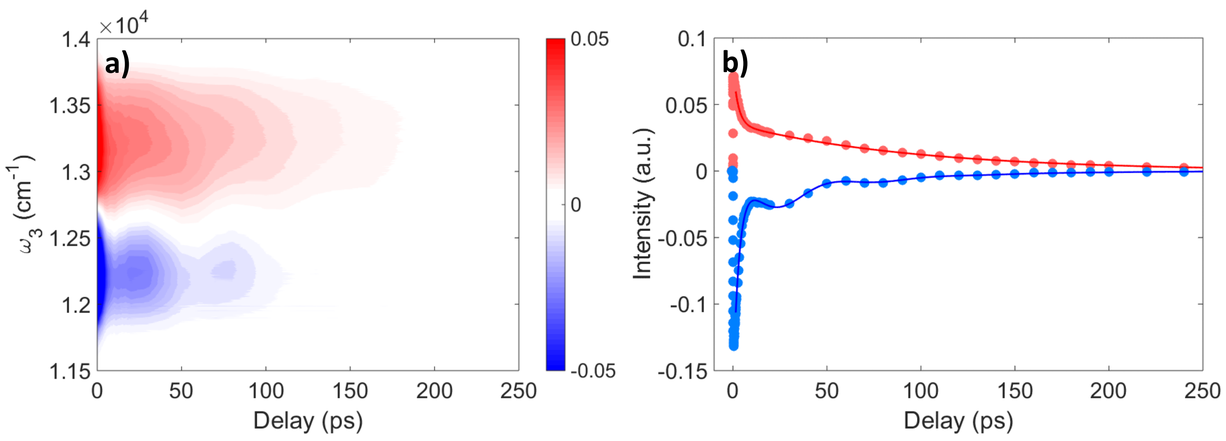


Figure 2: Normalized isotropic differential transmittance spectra ($\Delta T_{iso}/T_{iso}$) of AuNR collected at different delay between pump and probe ($FWHM_{pump}$ ~ 60 nm; $FWHM_{probe}$ ~ 80 nm) at different excitation wavelength: a) 780 nm; b) 760 nm; c) 740 nm.

Relaxation dynamics:

Figure 3: a) $\Delta T_{iso}/T_{iso}$ temporal evolution of the positive and negative bands after an excitation at 760 nm; b) Maximum and minimum temporal evolution of respectively the positive and negative bands of $\Delta T_{iso}/T_{iso}$. The positive band has been fitted by a bi-exponential decay, and the negative one by another bi-exponential decay modulated by a damped cosine.



	$\mathbf{0 \rightarrow 1}$	$\mathbf{1 \rightarrow 2}$
t_1	$2.63 \pm 0.09\ ps$	$3.4 \pm 0.2\ ps$
t_2	$95 \pm 2\ ps$	$60 \pm 5\ ps$
t_3	-	$25 \pm 5\ ps$
T	-	$56 \pm 4\ ps$

Table 1: Time constants of Fig2b) temporal evolution fitting.

2D ES:

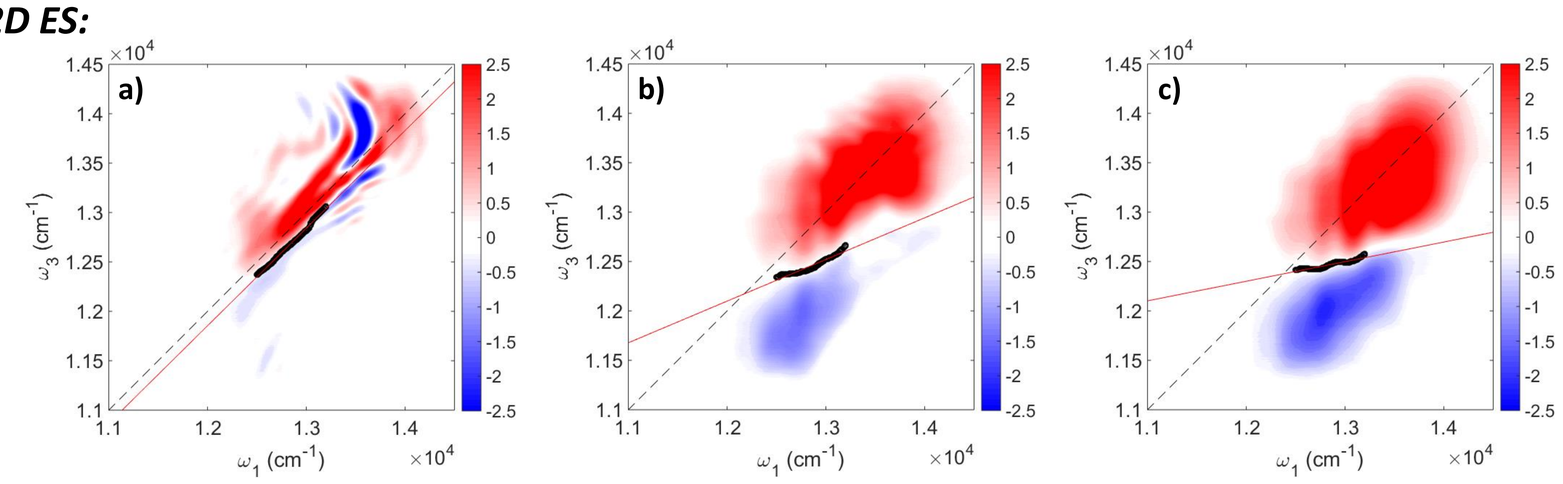


Figure 4: 2D ES spectra of AuNR at different waiting time: a) 0 fs; b) 150 fs; c) 1000 fs.

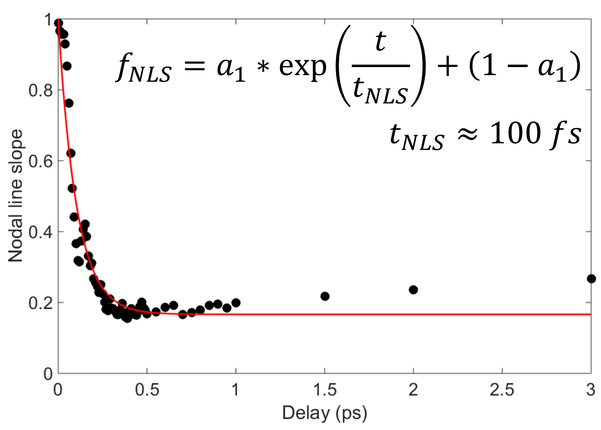


Figure 5: Nodal line slope temporal evolution.

CONCLUSION

We investigated the dynamics of AuNR using time-resolved 2DES technique. We observed 3 steps relaxation dynamic process. The first, the electron energy relaxation which is within in 90 fs, then the electron-photon coupling which occurs in ~ 3 ps, and finally the thermlisation with the environment which last several tens of picoseconds.