

Supporting information

Excitation Nature of Two-Photon Photoluminescence of Gold Nanorods and Coupled Gold Nanoparticles Studied by Two-pulse Emission Modulation Spectroscopy

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Preparation of Au nanospheres (Au NSs): Au NSs with an average diameter of 45 nm were prepared by citrate reduction of HAuCl₄.¹ Briefly, 1.5 mg HAuCl₄ was dissolved in 15 mL of H₂O and brought to boiling followed by addition of 0.12 mL of 1% sodium citrate solution. In ~30s the boiling solution turns faintly blue (nucleation) and the blue colour suddenly changes into a brilliant red after ~1 min, indicating formation of spherical Au particles.

Preparation of Au nanorods (Au NRs): Au NRs were prepared according to a previously reported seed-mediated growth method.^{2, 3} Gold seed solution was first prepared by mixing 5 mL of 0.1 M CTAB and 0.03 mL of 50 mM HAuCl₄. 0.1 mL portion of ice-cold 58 mM NaBH₄ was then added, which resulted in formation of a brownish-yellow solution. This brownish-yellow solution was kept at room temperature for at least 2 h. 0.2 mL of the gold seeds solution was subsequently added into the “growth solution” consisting of 100 mL of 0.1 M CTAB, 1.5 mL of 50 mM HAuCl₄, 0.224 mL of 50 mM AgNO₃ and 1.5 mL of 0.08 M ascorbic acid. The reaction mixture was left undisturbed overnight. The obtained Au NRs were purified by washing with deionized water to remove excess CTAB and re-dispersed in 70 mL of deionized water. These Au NRs have average width and length of 19 and 74 nm,

with an aspect ratio of 3.9. The extinction spectrum of Au NRs solution (**Fig. S1**) exhibited a transverse localized surface plasmon resonance (LSPR) band at 509 nm and a longitudinal LSPR band at 800nm.

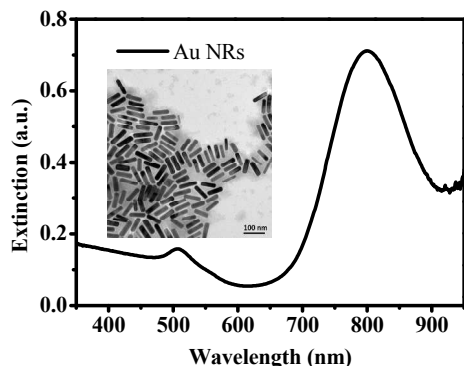


Figure S1. (a) UV-Vis extinction spectra and TEM images (inset) of Au NRs.

Instrumentations and Characterizations: Transmission electron microscopy (TEM) images of nanoparticles were taken from a Philips CM10 TEM microscope (at an accelerating voltage of 100 kV). Ultraviolet-visible (UV-Vis) extinction spectra were measured by using a SHIMADZU UV-2550 spectrophotometer. The two-photon photoluminescence measurements were performed by using a Avesta TiF-100M femtosecond (fs) Ti:sapphire oscillator as the excitation source. The output laser pulses have a central wavelength of 800 nm with pulse duration of 80 fs and a repetition rate of 84.5 MHz. The laser beam was focused onto the samples using a lens with a focus length of 3.0 cm. The emission was collected at an angle of 90° to the direction of the excitation beam to minimize the scattering. The emission signal was directed into a CCD (Princeton Instruments, Pixis 100B) coupled monochromator (Acton, Spectra Pro 2300i) with an optical fiber. A 750 nm short pass filter was placed before the spectrometer to minimize the scattering from the excitation light.

Two-pulse emission modulation experiments: The laser pulses were generated from a mode-locked Ti:sapphire oscillator seeded regenerative amplifier, which gives an output with a pulse energy of 2.0 mJ at 800 nm and a repetition rate of 1 kHz. The 800 nm laser beam was attenuated by neutral density filters before splitting into two

portions of approximately equal intensities. The two laser beams were focused onto the sample and spatially overlapped. One beam was modulated by an optical chopper at a frequency of 500 Hz. The time delay between these two pulse replicas was varied by a computer-controlled translation stage (Newport, ESP 300). The TPPL signals in the 500 to 700 nm range were collected by a Photomultiplier tubes (Hamamatsu R928) attached to a monochromator (Acton SP-2150i, PI). The PL signals are recorded as a function of the time delay of the two pulses.

Pump-probe experiments: Pump-probe measurements were performed on Au NRs and coupled Au NSs by using the same femtosecond laser system. The experimental setup is shown in Fig. S2. Briefly, the 800 nm laser beam was split into two portions. The larger portion of the beam was used as the pump beam. A residual portion of the beam was used to generate white light continuum (WLC) in a 1 mm sapphire plate. The WLC was split into two beams, one as probe and the other as a reference to correct for pulse-to-pulse intensity fluctuations. The signal and reference beams were detected by photodiodes that are connected to lock-in amplifiers and the computer. The pump beam is focused onto the film with a beam size of 300 μm and overlaps with the smaller diameter (100 μm) probe beam. The delay between the pump and probe pulses was varied by a computer-controlled translation stage (Newport, ESP 300). The pump beam was modulated by an optical chopper at a frequency of 500 Hz. The variation transmittance at selected probe wavelength is recorded as a function of time delay between pump and probe pulses.

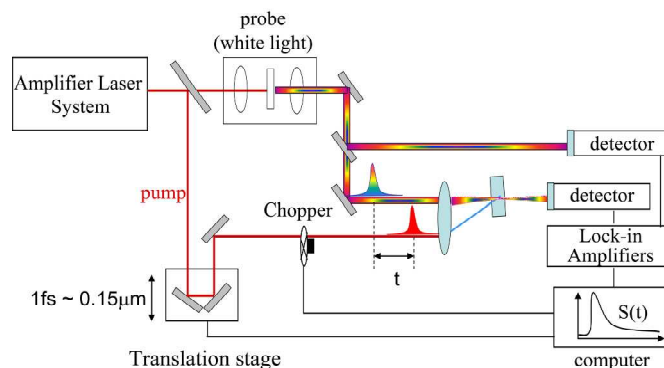


Figure S2. Experimental setup for pump-probe measurements.

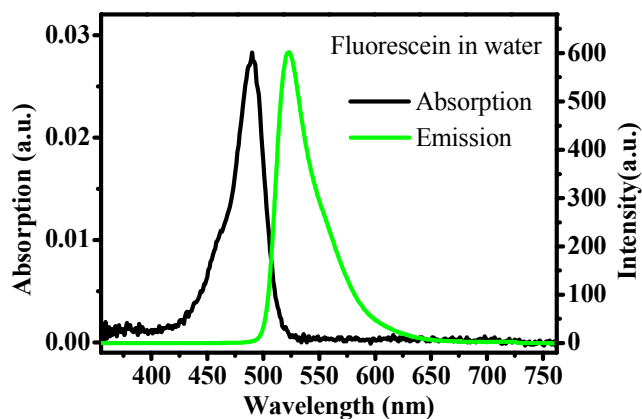


Figure S3. Absorption and fluorescence spectra of fluorescein in water (pH adjusted to 11 by using proper amount of NaOH)

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