

Relative Enhancement of Ultrafast Emission in Gold Nanorods

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Time-resolved fluorescence spectroscopy has been employed to probe the ultrafast emission observed in gold nanospheres and nanorods. The decay of the emission was found to be ≤ 50 fs. The ultrafast emission from nanorods has been directly compared to that for nanospheres and the dispersion of the relative local field enhancement factor was obtained and compared with calculations. Measurements with both visible and ultraviolet excitations have been analyzed. These results give the first observation and analysis of the mechanism for the local field-enhanced ultrafast emission in gold nanorods and nanospheres.

The optical properties of metal nanoparticles have attracted a wide degree of interest due to possible applications in nanotechnology.^{1,2} In terms of the details of the optical excitations of metal nanostructures with different geometries, there has been many important investigations regarding the excitation and subsequent relaxation processes.^{3–5} Understanding the details of such processes is not only of fundamental interest but may also give information regarding applications in surface-enhanced Raman scattering,⁶ nonlinear optics,⁷ and surface-enhanced fluorescence.⁸

Electron dynamics in small metal nanoparticles probed by the femtosecond transient absorption spectroscopy has been a subject of extensive research.^{3–5,9} This method made it possible to monitor processes such as electron thermalization, electron cooling, and decay at high electron temperatures. For example, the thermalization time of an initial non-Fermi electron distribution in gold nanoparticles was estimated to be about 500 fs.⁹ This is close to that measured in gold films by a similar method¹⁰ or by a photoelectron emission spectroscopy.^{11–13} Gold nanorods and nanospheres are two particular types of metal nanoparticles that have recently attracted great attention in investigations of the particle-shape effects on optical excitations.³ Light-scattering investigations have been carried out with single nanorod particles and a “drastic” reduction of the plasmon dephasing rate in the rods (in comparison to nanospheres) was observed.¹⁴ The reason for this reduction was suggested to be the suppression of interband damping for longitudinal resonance.¹⁴ There have also been reports of surface-enhanced Raman scattering with metal nanorods,¹⁵ as well as on excitation of anisotropic coherent vibrational motions in such systems.¹⁶ However, there have been only a limited number of reports of the time-resolved emission in gold metal particles,¹⁷ and no report of ultrafast emission in gold nanorods. While there have been reports of enhanced continuous wave (CW) fluorescence in gold nanorods,^{3,18} many important features of the emission processes in these systems remained to be understood.

Detailed investigations of the time-resolved emission in gold nanorods and nanospheres are important because they can lead

to a better understanding of the enhancement process that is observed in different metal geometries and may further lead to information regarding the actual mechanism of emission in gold particles. The two principle processes that may lead to emission in gold nanoparticles are (1) direct (intraband) excitation of the surface plasmon resonance and emission from this collective electron motion^{19,20} and (2) excitation of an interband transition followed by electron–d-hole recombination emission, which is enhanced by a strong local field in the vicinity of the longitudinal surface plasmon resonance for the case of gold nanorods.²¹ It is interesting to note that it has been nearly 3 decades since Mooradian first described the very inefficient (10^{-10}) fluorescence in metal yet there still remains a basic question as to the dynamics of the emission process.²²

In this letter, we present the results of relative enhancement of ultrafast emission in gold nanorods of different aspect ratios. The results from the rods are systematically compared to gold nanosphere results. The dispersion of the ultrafast emission enhancement in nanorods relative to that in nanospheres is measured and compared with the calculated spectrum. Measurements at two different excitation regimes indicate that the fast emission is not sensitive to the wavelength of excitation and the efficiency of the emission is nearly the same at both excitation regimes. The time-resolved emission is further analyzed in view of certain electron–electron scattering mechanisms. These results give a systematic insight into the enhancement and mechanism of ultrafast emission in gold metal particles of different geometries.

The particles investigated here were produced by an electrochemical method described previously in the literature.¹⁸ The gold nanospheres (SP) used for these investigations had an average diameter of 25 nm. The gold nanorods of different aspect ratios were prepared in micellar form as outlined in the literature,¹⁸ and measurements were carried out in aqueous solution at room temperature. Two gold nanorod samples were used in these investigations. The first (NR1) has an average diameter of 15 nm and a length of about 35 nm (corresponding aspect ratio 2.7) as determined by the analysis of TEM images. The second sample (NR2) contains gold nanorods with an average diameter of 15 nm and a length of around 28 nm (corresponding aspect ratio 1.8). The samples SP and NR1 have almost matching optical densities at 400 nm (0.148 and 0.149

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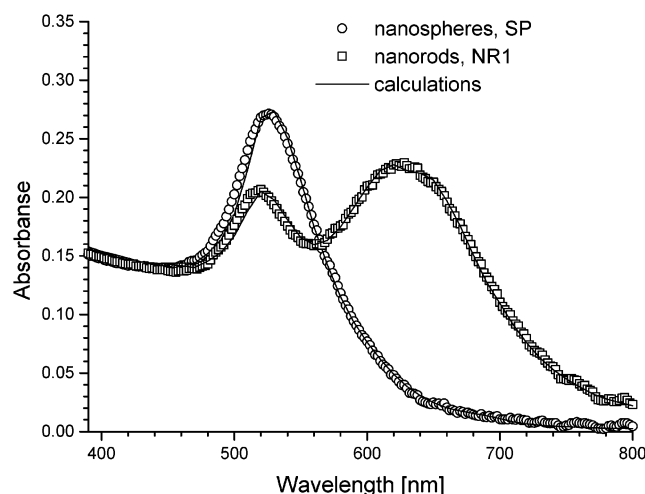


Figure 1. Absorption spectra of nanospheres (SP) and nanorods (NR1). The corresponding numerical fits to the data are indicated by the solid lines.

in 1 mm cell), which is important for direct comparison of the emission excited at this wavelength in nanorods and nanospheres. The ultrafast measurements were carried out with a femtosecond upconversion unit as described in previous reports.^{17,23} The fundamental (800 nm, 40 fs, 82 MHz) pulse was frequency-doubled (and -tripled) to give excitation pulses in visible and UV. The fluorescence upconversion unit has an instrument response function of 180 fs, and this system also has the capability to carry out ultrafast emission anisotropy decay measurements. For the measurements of the spectrum of the fast emission component, the setup has been calibrated using several standard dyes. The energy per excitation pulse did not exceed 600 pJ.

Shown in Figure 1 is the linear absorption spectrum for the gold nanospheres and gold nanorods (NR1). The spheres show a single surface plasmon resonance near ~530 nm. The absorption spectrum of gold nanorods NR1 is characterized by two bands: a transverse plasmon resonance near ~530 nm and a longitudinal resonance near 630 nm. The study of individual gold nanorods¹⁴ showed that the optical spectrum of a single nanorod can be well described by the Gans extension of the Mie theory²⁴ using the bulk dielectric function of gold without adjustable parameters and neglecting the surface effects.¹⁴ To model the absorption spectrum of our samples, which contain an ensemble of nanorods (lengths), we introduced a distribution of aspect ratios (adjustable) around the values estimated by TEM (1.8 or 2.7) and used the Gans expression for the extinction of randomly oriented nanorods.^{24,3} The bulk dielectric function of gold was taken from the measurements on gold films under vacuum conditions,²⁷ and the dielectric constant of the surrounding medium, $\epsilon_m = 2$, was used in calculations. The best fit results of these calculations for samples SP and NR1 are shown in Figure 1. The calculated spectrum for NR1 corresponds to a distribution of rod lengths centered at ~2.9 aspect ratio with some contribution of the spheres.²⁸

Shown in the inset of Figure 2 is a typical time-resolved fluorescence trace that we obtained from fluorescence upconversion measurements of the gold nanorods NR1. The observed emission (excited at 400 nm) is very fast, and it is easily seen from the figure that it is faster than our instrument response function. Estimation of the decay time by deconvolution procedures resulted in an emission decay time ≤ 50 fs. A very weak, long-lived component is also seen. The origin of this component is not completely clear at the moment. It is worth

noting that the emission intensity was strictly linearly dependent on the excitation power in the power range that we used for excitation. The measured fast emission dynamics is similar for both gold nanorods and gold nanospheres, and it is not dependent on the emission wavelength within the time resolution of the instrument. Further investigations with both gold nanorods and gold nanospheres also showed that when UV excitation pulses are used the same fast dynamics of the observed emission was obtained. Ultrafast anisotropy measurements were also carried out at both excitation regimes. It was found that the ultrafast emission is depolarized with a residual anisotropy value close to zero (not shown), as was also the case of gold-dendrimer nanocomposites.¹⁷

Shown in Figure 2 is the fast emission spectrum of nanospheres obtained with 410 and 267 nm excitations. The results are normalized to the same number of absorbed photons for both excitation wavelengths. It is clearly seen that the fast emission peak emerges at about 530 nm independently of the excitation wavelength. This gives strong evidence that the observed emission is a real luminescence from the relaxed state rather than scattering. The fact that the quantum efficiency of the emission excited at 267 nm is about the same as that for excitation at 410 nm, as well as the depolarized character of the emission, is inconsistent with the suggestion that the observed emission stems from the surface plasmon dipole emission after direct surface plasmon excitation by incoming field. We consider the observed ultrafast emission originating from sp-electron–d-hole recombination with the enhancement of the incoming and outgoing fields via plasmon resonances as it was proposed for the steady-state emission from copper and gold.^{18,21,22} Thus, a comparison of the fast emission from the samples SP and NR1 having the same absorption at 400 nm allows us to directly measure the dispersion of the enhancement factor of nanorods (NR1) relative to that of nanospheres (SP).

Shown in Figure 3a is the relative enhancement spectrum for the gold nanorods NR1 relative to that of nanospheres (SP). As it can be seen from the figure, the enhanced emission of the rods is easily observed at longer wavelengths, and the enhancement relative to that for the sphere is more than 1 order of magnitude. Also shown in Figure 3a, is the calculated relative enhancement factor. The calculated line is based on the local field enhancement factor initially derived for the oriented semispheroid with lightning rod factor, L_{LR} , given as^{21,26}

$$L(\omega) = \frac{L_{LR}}{\epsilon_1(\omega) + i\epsilon_2(\omega) - 1 + L_{LR} \left(\frac{1 + 4\pi^2 i V [1 - \epsilon_1(\omega) - i\epsilon_2(\omega)]}{3\lambda^3} \right)} \quad (1)$$

where ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant taken from ref 27 and λ is the wavelength of emission. In our numerical calculations, we additionally take into account the random orientations of the spheroids and the distributions of the aspect ratios (or L_{LR}), which were obtained from the fitting of absorption spectra mentioned above. We calculated the enhancement factor for incoming field at 400 nm and dispersion of the enhancement factors for outgoing fields and took the ratio of intensity enhancements for nanorods (NR1) and nanospheres (SP). No other adjustable parameters are used. The agreement of the experiment with this simple model of local field enhancement is quite remarkable. Also shown in Figure 3b is the result for the samples SP and NR2. To better observe the result, the calculated curve is rescaled to match the experimental

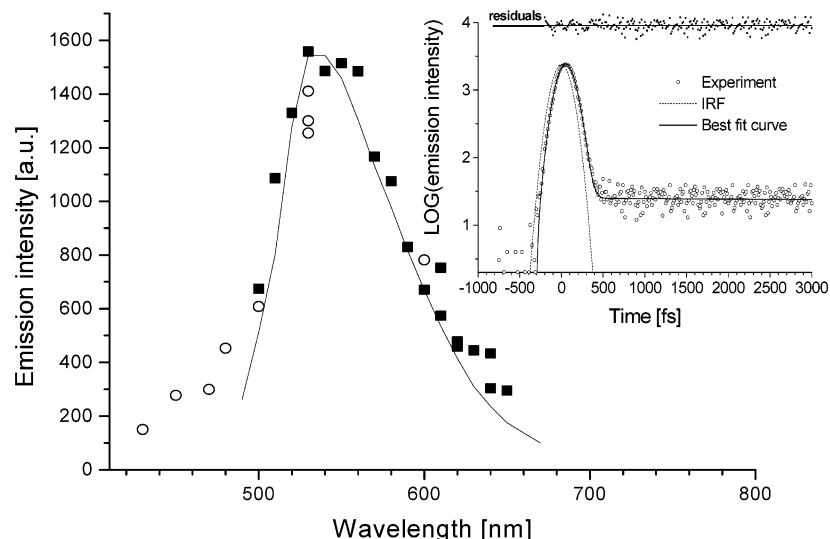


Figure 2. Spectrum of the fast component of gold nanospheres (SP): (■) excitation at 410 nm (3.02 eV); (○) excitation at 267 nm (4.65 eV). The insert displays the time-resolved emission from nanorods NR1. The best fit curve and instrument response function are also shown.

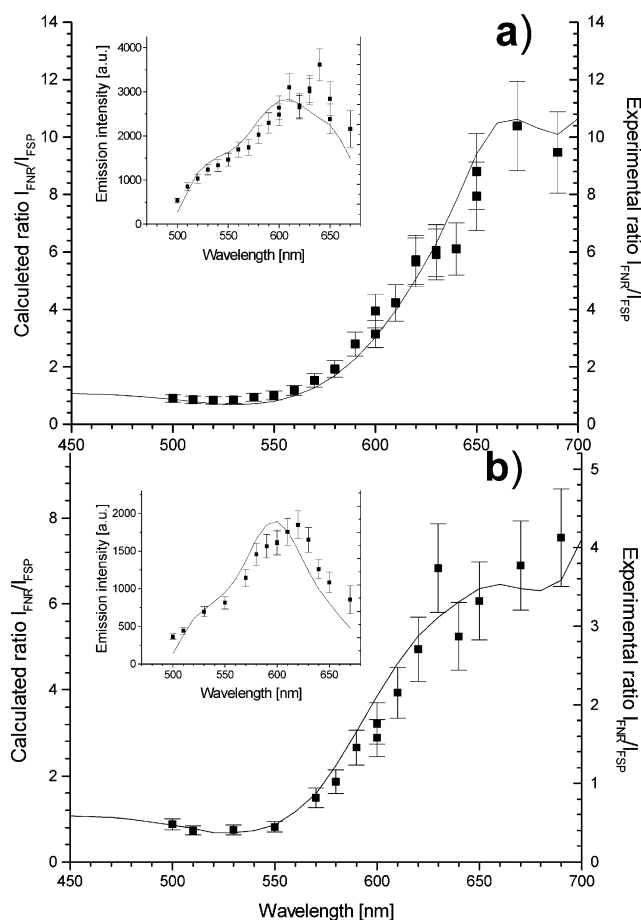


Figure 3. The ratio of the emission intensity of nanorods (a) NR1 and (b) NR2 to that of nanospheres. Spectra of the fast component of gold nanorods are shown in the respective insets. The result of numerical calculations for each case is also shown (see text for details).

ratio at 530 nm in the figure. Interestingly, this rescaling factor is about the ratio of optical densities of SP and NR2 samples at excitation wavelength, which is in agreement with the simple model described above. It should be noted that while this result is not many orders of magnitude of enhancement for these particular samples in comparison to the spheres as one may have found immediately very advantageous for the sake of applica-

tions, it does agree well with theoretical predications and can be used as a direct demonstration and model of the enhancement process of emission in future metal nanostructures.

Shown in the inset of Figures 3a,b is the spectrum of the ultrafast emission for the gold nanorods NR1 and NR2, respectively. Both spectra show the broad peaks near the longitudinal SP resonance and the shoulder at about 530 nm. Also shown in the insets are the calculated emission spectra for both nanorod samples. Initial recombination emission spectrum for bulk gold is taken either from Mooradian's experiment²² or from a theoretical model developed by Apell et al.²⁵ (which are very close to each other). This spectrum has been multiplied by the enhancement factor calculated in accordance with the procedure described above. The result of these calculations fits relatively well to the experimental wavelength dependence of the ultrafast emission. Also shown in Figure 2 is the emission spectrum from the gold nanospheres calculated using the procedure described above for nanorods. All of these fits with our experimental data may give further evidence of an electron-d-hole recombination mechanism of the observed ultrafast emission.

As mentioned above, various suggestions have been attributed to the understanding of emission and absorption in gold nanoparticles. Some of the discussions have centered on the thermalization process of the non-Fermi distribution of electrons to a Fermi distribution, which may occur on a time scale of hundreds of femtoseconds.⁹⁻¹³ Interestingly, the ultrafast emission observed here with both the gold nanorods and gold nanospheres occurs on a time scale of 50 fs (or faster) without detectable delay after excitation even for the excitation far above Fermi level (267 nm, $\omega_{\text{exc}} = 4.65$ eV). This suggests that the formation and thermalization of "hot" electrons in the excitation process may not be contributing processes to the emission that we have investigated. Instead the emission is strongly related to the dynamics of the d-holes created immediately after excitation. The interesting conclusion of our measurements is that the hole relaxation within d-band in momentum space to meet the momentum conservation for the radiative recombination for the electron near the Fermi level^{21,22,35} proceeds extremely fast resulting in no detectable delay in the appearance of the emission in our experiment. It is also possible that the confinement in small particles lifts the strict momentum conservation requirement and makes the immediate recombina-

tion feasible. The lifetime of the recombination emission is limited by the lifetime of the d-holes. Although recent two-photon photoemission studies indicated that the holes in noble metals exhibit considerably longer lifetimes than electrons of the same excitation energy, the electron–electron scattering into the empty states into the d-band holes remains on time scale less than 100 fs.^{12,13} The fast nonradiative hole filling process most likely happens through the process similar to the Auger process because of energy conservation for electro-electron scattering and it may lead to highly excited nonthermal electrons.^{9,21,25} The lifetime of d-holes was estimated for copper to be about 20–30 fs.^{12,13} Our time-resolved emission measurements can give the upper limit of the lifetime of d-holes in gold nanoparticles as about 50 fs.

In summary, we have shown that the ultrafast emission observed in gold nanorods of different aspect ratios is relatively enhanced in the vicinity of the longitudinal surface plasmon resonance. The enhancement reached more than 1 order of magnitude for the case of the gold nanorods with average aspect ratio 2.7. The observed ultrafast emission spectra and the spectra of enhancement agree well with the theoretical predictions of local field enhancement factors. The observed ultrafast emission is depolarized and does not appear to involve such processes as the thermalization of hot electrons. These results may draw closer attention to the possibility of enhanced fluorescence in metal nanoparticles of different geometries, as well as understanding of the basic processes of emission in metal particles.

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