

Optical properties of silver nanoprisms and their influences on fluorescence of europium complex

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Abstract: The optical properties of truncated triangular silver nanoprisms and their influences on the fluorescence of europium complex $\text{Eu}(\text{TFA})_3$ were investigated in theory and experiment separately. In theory, we found that the fluorescence of Eu ions would be greatly enhanced by these nanoprisms, the enhancement factor of the fluorescence depended on the concentrations of nanoprisms. They were verified in the experiment. The influence of silver nanoprisms on the radiative and nonradiative decay rates of Eu ions were also deduced, and found that the silver nanoprisms greatly reduced the energy loss caused by the nonradiative decay.

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1. Introduction

Rare earth (RE) doped optical materials have been widely researched and used in many fields. It is a permanent effort to improve the emission efficiency of the RE doped materials. Many works on luminescence enhancement of RE optical materials by surface plasmons have been reported, among which metal nanoparticles have attracted many attentions due to their special properties [1–5]. The local surface plasmon resonance (LSPR) of nanoparticles can be tuned by changing the size, shape, interparticle spacing, and dielectric environment of nanoparticles [6–11], which making the nanoparticles become a powerful media for adjusting the performance of the RE doped materials [1,3,12–16]. However, the mechanism of the enhancement by LSPR is still not very clear, especially the detailed influence of LSPR on the radiative and nonradiative decay rates of RE ions.

In this work, we synthesized the truncated triangular silver (Ag) nanoprisms (NPs) by the chemical method, and their side length and thickness were about 80nm and 16nm separately. In theory, we calculated scattering properties of this kind of NPs and suggested some ideas about their influence on the luminescence of europium complex $\text{Eu}(\text{Ttfa})_3$. In experiment, we compared the luminescence of with or without Ag NPs, and found that the luminescence at 612nm was obviously enhanced and the enhancement factor depended on the concentrations of the Ag NPs. The experimental results coincided with the theoretical suppositions. In addition, we also deduced the influence of Ag NPs on the radiative and nonradiative decay rates of Eu ions, and found that the NPs greatly reduced the energy loss caused by nonradiative decay.

2. Experiments and Calculations

2.1 Experimental Details

A. Samples preparation The Ag NPs were synthesized by chemical method [17]. In a typical experiment, spherical Ag nanoparticles were prepared by injecting ice-cooled NaBH_4 (10mM, 1ml) as drop-wise addition to an aqueous solution of AgNO_3 (10mM, 1ml) containing trisodium citrate solution (10mM, 3ml). The color of the colloid solution was pale yellow. Next Polyvinylpyrrolidone solution (PVP) (0.4ml, 6mg/ml) as a particle stabilizing agent was added to the 10ml precursor solution. To eliminate the possibility of oxidation of nanoparticles, all the experiments were performed in a nitrogenous atmosphere. The system was then irradiated with a conventional 40W fluorescent light for 70 hours. Finally the color of the solution appeared to be blue. The nanoprisms were subsequently centrifuged by Hermite Z323 at 13000rpm to remove excess PVP and redispersed in deionized water.

$\text{Eu}(\text{Ttfa})_3$ was dissolved into absolute ethanol with a weight ratio of $\text{Eu}(\text{Ttfa})_3$:ethanol = 0.68%. Different volume of prepared Ag NPs colloids was mixed into the solution of europium complex. To ensure the same content of deionized water in our solution, different volume of deionized water was added to the solution, finally the samples we used were obtained.

B. Spectra Measurement Scanning electron microscopy (SEM) was used to observe the average size of the NPs. The absorption spectra of the NPs were taken with a *Perkin Elmer*

UV-visible-NIR Lambda 19 Spectrophotometer. The emission spectra were obtained by *Jobin Yvon Fluorolog-3 Spectrophotometer System*. All the samples were excited at the wavelength of 350nm, at which the ligand TTFA had a strong absorption. In our experiments, we focused on the electric dipole transition of ${}^5D_0 \rightarrow {}^7F_2$ at 612nm, because this electric-dipole transition is more sensitive than other magnetic-dipole transitions to the variation of local environments due to the addition of Ag NPs. For the lifetime measurements, the fluorescence decay curve using the technique of time-correlated single photon counting (TCSPC) was obtained by the *FluoroHub-B*, which is an integral component of a typical *HORIBA Jobin Yvon photon counting lifetime system*. The fluorescence decays are analyzed using the *HORIBA Jobin IBH's flagship software DAS6*.

2.2 Computational Details

Scattering were calculated for describing the NPs' properties by using the finite-difference time-domain (FDTD) software *FDTD solution 6.5*. Our simulation parameters based on the experimental results. The calculations are made in 3 dimensions. The incident light is a plane wave with a wavevector normal to injection surface and propagates along the x direction, and it passes midway through the nanoprisms.

3. Theory on plasmon-enhanced luminescence of fluorophores

The luminescence intensity I_F of organic fluorophores at a certain emission wavelength is [18]:

$$I_F = 2.3I_0\varepsilon(\lambda)clQ_0, \quad (1)$$

where I_0 is the intensity of the incident light, $\varepsilon(\lambda)$ is the dielectric constant at a precise emission wavelength, c is the velocity of light, l is the thickness of the sample, and Q_0 is the quantum yield. For our samples, the influence of Ag NPs on $\varepsilon(\lambda)$ can be ignored because of their quite low volume fraction [19]. c and l are constant. So the LSPR originating from the Ag NPs can influence the luminescence of RE ions by two parameters [4,20]: the intensity I_0 and the quantum yield Q_0 , which are usually called as the excitation enhancement G_{ex} and the emission enhancement G_{ra} [21], respectively. And the LSPR can be characterized by the extinction (including absorption and scattering) spectrum of the nanoparticles. For the excitation enhancement G_{ex} , Ag NPs absorb energy of the incident light and generate the LSPR which can realize the enhancement of the local electric field. The intensity of the local electric field at the location of the dipole, is therefore obtained as the sum of the original incident beam and the influence of the LSPR, that is [22]:

$$I = I_0 + \sum_{j=1}^N I_{np}, \quad (2)$$

where the $\sum_{j=1}^N I_{np}$ is the secondary electric field caused by the LSPR of the Ag NPs. The G_{ex} has a great relationship with the enhanced local electric field which depends on the overlap between the LSPR spectrum of NPs and the absorption band of Eu ions [22]. For the emission enhancement G_{ra} , the quantum yield (Q_0) and lifetime (τ_0) of an excited fluorophore in a free space can be expressed as follows [18]:

$$Q_0 = \frac{\Gamma}{\Gamma + K_{nr}},$$

$$\tau_0 = \frac{1}{\Gamma + K_{nr}},$$
(3)

where Γ is the radiative decay rate and K_{nr} is the nonradiative decay rate of the fluorophore, respectively. For a fluorophore near metal nanoparticles, the excited fluorophores can transfer their energy to the metal nanoparticles and excite the LSPR, if appropriate. In turn the LSPR can transform into the emission light with certain efficiency. In this process, both the Γ and K_{nr} of RE ions might be altered, and further leading to the emission enhancement if the conversion efficiency from LSPR to emission light is higher than the intrinsic emission efficiency of fluorophores. Some researchers have pointed out that the emission enhancement could be shown by the overlap between the emission spectrum of RE ions and the scattering spectrum of NPs [23]. The way of the influence on the emission process can be understood as the energy transfer from the excited state Eu ion to the LSPR, which then radiate to the far-field and result in the increase of fluorescence. The NPs also can mediate the emission light by increasing the coupling of the emission light and scattering of the NPs. Separating out these two ways of the influence on the emission process is difficult, however, they both depend on the overlap between scattering band of NPs and emission band of Eu ion, thus they are both called the emission enhancement G_{ra} [24].

4. Results and Discussion

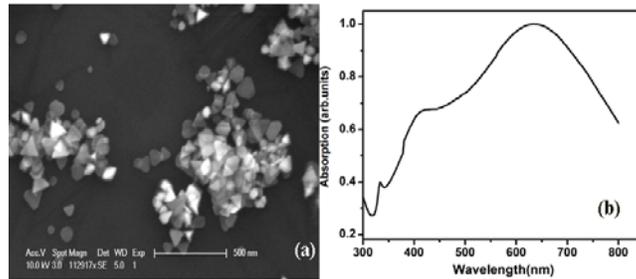


Fig. 1. The SEM image (a) and the absorption spectrum (b) of the Ag NPs.

Figure 1 is the SEM image and the absorption spectrum of the Ag NPs, most of them are truncated triangles, with the side lengths of about 80 ± 20 nm and the thicknesses of about 16 ± 2 nm. The UV-visible absorption of the triangular NPs centers at about 635 nm, the absorption at excitation wavelength is very weak.

To deduce the excitation enhancement of Ag NPs, we calculated the local field distribution around a truncated Ag NP at the wavelengths of 350 nm and 612 nm separately. Figure 2 is the local electric field enhancement around the Ag NP, the color bar shows the enhancement factor of the local electric field. At the excitation wavelength, the local field enhancement multiplies several times. At the emission wavelength, the enhancement even reaches to hundred times.

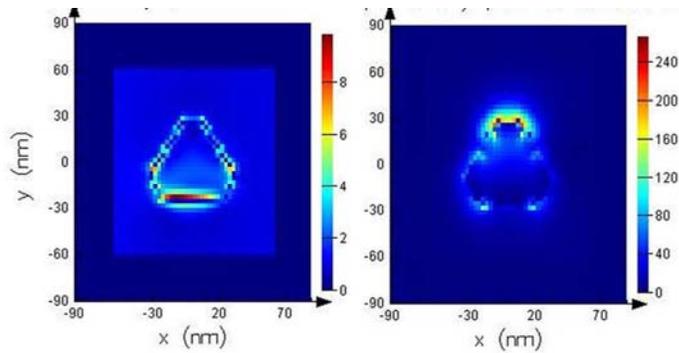


Fig. 2. The local electric field enhancement of the triangular Ag NP for the x-y plane. The incident light propagates along the x direction and it passes midway through the prism. The left is at the excitation wavelength 350nm. The right is near the emission wavelength of 612nm.

To further find out the emission enhancement of Eu ion, the scattering spectra of Ag NPs is studied, we also calculate the scattering properties of NPs by the FDTD method. Figure 3 shows the scattering spectra of a single NP and two interacted NPs with different distances (10nm, 2nm, 0nm). For a single NP, the scattering spectrum centers at about 610nm, this is very close to the emission wavelength of Eu ions. For the two interacted NPs, the intensity of the scattering field increases and the position of the peak red shifts by 150nm while their distance decreases. The scattering spectrum splits to two peaks when the two NPs are near enough. So the scattering spectrum can be tuned by varying the distance between NPs, which is very consistent with the result in Ref [20].

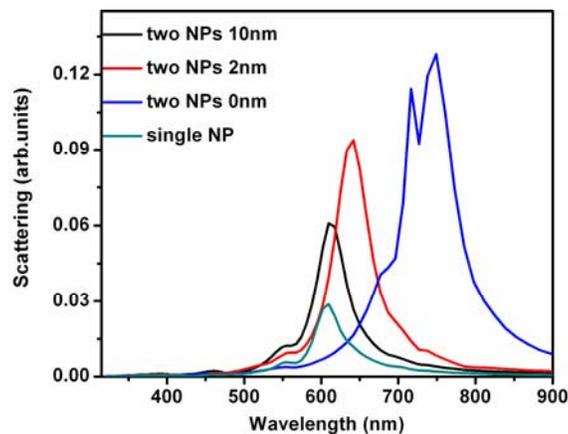


Fig. 3. The scattering field in different conditions. The green, black, red and blue lines show the scattering of the single NP and two NPs with the distances of 10nm, 2nm and 0nm, separately.

Based on the above results, we know that the Ag NPs we used could not obviously enhance the excitation of Eu ions at 350nm, but greatly influence the emission process from the Eu luminescence centers. And according to the adjustable scattering spectra, we note that the influence of the NPs would depend on the concentrations of NPs. We would verify these suppositions in experiment next.

In experiment, the 575-665nm band photoluminescence spectra of europium complex $\text{Eu}(\text{TtFA})_3$ with different concentrations of Ag NPs excited by 350nm are shown in Fig. 4. The inset shows the dependence of the enhancement factor on the NPs' concentrations. From this figure we can see that the luminescence of Eu ions enhances greatly due to the Ag NPs. As the figure shows, when the concentration of Ag NPs increases, the enhancement factor gradually

increases until it reaches a maximum and then decreases. The optimum luminescence is obtained by the adding 1.10ml Ag NPs colloid, the maximum enhancement factor is about 5.5.

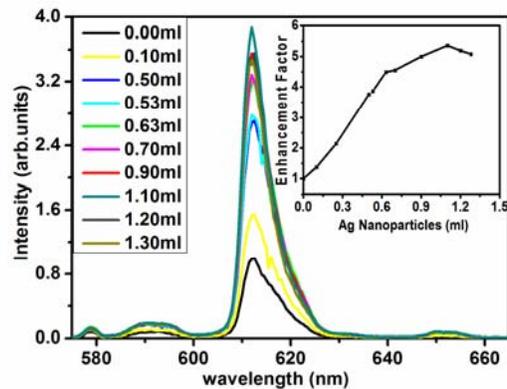


Fig. 4. The photoluminescence spectra of europium complex $\text{Eu}(\text{TTFA})_3$ with the different volumes of Ag NPs. Inset shows the enhancement factor dependence on the concentrations of NPs at the emission wavelength of 612nm.

From the mentioned theory above, the emission enhancement can be shown by the overlap between the emission band of Eu ions and the scattering spectra of NPs [23]. As shown in Fig. 3 and Fig. 4, when the distance of NPs decreases, the scattering at 612nm firstly increases, which makes the increase of the overlap between the scattering of Ag NPs and the emission band of Eu ions and results in the enhancement of luminescence. Then it decreases as the distances between NPs further decrease, which result in the decrease of coupling efficiency between the Ag NPs and Eu ions, and the decrease of the enhancement factor of luminescence. The results shown in Fig. 4 bear out the above suppositions.

To further prove the influence of Ag NPs on the emission, we also measured the lifetime of europium complex $\text{Eu}(\text{TTFA})_3$ at 612nm with different concentrations of Ag NPs. As shown in Fig. 5, the variation of lifetime also depends on the concentrations of Ag NPs. Firstly the lifetime is $147 \mu\text{s}$ in absence of Ag NPs, then it increases with the adding of the Ag NPs, and the maximum of the lifetime reaches $260 \mu\text{s}$ when 1.10ml Ag NPs colloid is added, finally the lifetime decreases with the further addition of the Ag NPs. Its variation trend is similar with that of enhancement factor of luminescence in Fig. 4. This result is different from the previous result [1].

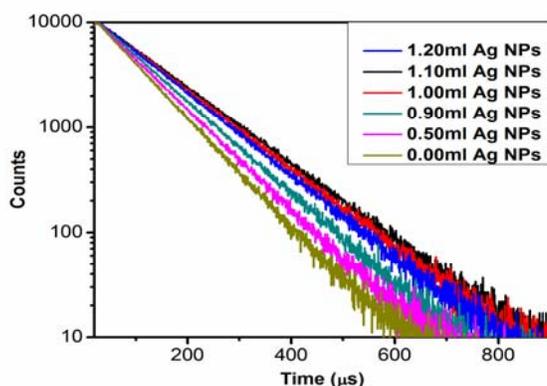


Fig. 5. The lifetime of europium complex $\text{Eu}(\text{TTFa})_3$ at 612nm with the different concentrations of Ag NPs.

The quantum yield Q_0 would increase due to the mainly influence on the emission process of Eu ions. However, the lifetime τ_0 of Eu ions at 612nm also increases in presence of Ag NPs from the result in Fig. 5. For the radiative decay rate, as we know, the intensity ratio from ${}^5D_0 - {}^7F_2$ to ${}^5D_0 - {}^7F_1$ is usually treated as a prober for detecting local crystal field, because of the greater sensitivity to the variation in local environment surrounding europium ions for the electric-dipole transition than that for the magnetic-dipole transition [25], so we can obtain the relative change of the radiative decay rate by this ratio. In our case, the change of this ratio notes that the radiative decay rate Γ increases. According to the Eq. (3), we can deduce that the nonradiative decay rate K_{nr} decreases, moreover the decreasing extent of the nonradiative decay rate is greater than the increasing extent of the radiative decay rate. This result means that the addition of Ag NPs can reduce the energy loss caused by nonradiative decay K_{nr} . To the extent of our knowledge, no papers has involved the influence on the nonradiative decay rate before except a recent report Ref [25].

5. Conclusion

In summary, we demonstrated that the NPs we used was the efficient enhancement structure for the luminescence of $\text{Eu}(\text{TTFa})_3$ both in theory and in experiment. The obvious enhancement of luminescence at the emission wavelength of 612nm was obtained. Also we explained why the enhancement of luminescence depended on the concentrations of the NPs by using the NPs' scattering property. When the overlap between the LSPR band of NPs and the emission band of fluorophore was well, the NPs had a greater influence on the emission process, and the nonradiative decay energy loss could be greatly decreased by the LSPR of the NPs, which made a greater enhancement of the luminescence. Based on these calculation and experimental results, in order to obtain a great enhancement of the luminescence, we should increase the absorption of the nanoparticles at the excitation wavelength of the phosphor for increasing the excitation enhancement, and increase the scattering of the nanoparticles at the emission wavelength of the phosphor for increasing the emission enhancement, separately. It is difficult to realize the two aspects at the same time by using a single kind of nanoparticles. This might be the reason that the enhancement of the luminescence by using nanoparticles is not very great so far. If we could synthesize two or more kinds of appropriate nanoparticles simultaneously, the luminescence enhancement of the fluorophore would be better.

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