

纳米银对铕配合物荧光性质的影响

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摘要: 研究了纳米银对稀土铕-吡啶-2,6-二羧酸配合物($\text{Eu(III)C}_7\text{H}_5\text{NO}_4$, Eu(III)DPA)的荧光性质的影响。随着纳米银浓度增加, 荧光强度先增强而后逐渐下降。较大粒径的纳米银使 Eu(III)DPA 荧光增强效率较大, 且达到最大荧光增强效率所需的纳米银浓度较低。在高浓度 Eu(III)DPA 溶液体系中, 纳米银导致荧光猝灭。电偶极子跃迁发射荧光增强效率大于磁偶极子跃迁发射荧光增强效率。分析认为, 纳米银对 Eu(III)DPA 荧光性质的影响与表面等离子体共振与激发态荧光中心强烈耦合以及表面等离子体再吸收有关。同时, 纳米银对铕配合物的不对称率有影响, 其影响因素与局域电磁场增强, 折射率以及配位场有关。

关键词: 铕配合物; 纳米银; 荧光增强; 表面等离子体共振; 局域电磁场

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Effects of Silver Nanoparticles on the Luminescent Properties of Europium Complex

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Abstract: A detailed study of the effects of silver nanoparticles on the luminescent properties of the europium complex ($\text{Eu(III)C}_7\text{H}_5\text{NO}_4$, Eu(III)DPA), where DPA is dipicolinic acid, in the aqueous solution system was reported. The emission intensity of the Eu(III)DPA solution initially increased with increasing of the amount of silver colloids and then decreased. The large silver nanoparticles resulted in the high enhancement efficiency and the low amount at which the enhancement efficiency reaches the maximum. The emission intensity was quenched by silver nanoparticles in high concentration of Eu(III)DPA solution. The enhancement for the emission of electric dipole transition was stronger than that of magnetic dipole transition. The observed silver nanoparticles dependences of the luminescent intensity were regarded as the result of a stronger coupling between the surface plasmon resonance and the excited luminescence centers and re-absorption of surface plasmon resonance of silver nanoparticles. Meanwhile, the asymmetric ratio of the europium luminescence affected by silver nanoparticles was discussed in terms of the local electromagnetic field enhancement, refractive index, and the ligand field around europium ion.

Key words: europium complex; silver nanoparticles; luminescence enhancement; surface plasmon resonance; local electromagnetic field

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Metal-enhanced fluorescence (MEF) effects of metal nanostructures on different luminescent materials have been received considerable attention for their scientific significance and applications in medical diagnostics and biotechnology^[1-2]. It is known that the emission intensity can be enhanced to $10 \sim 10^3$ -fold by a near-field interaction of a fluorophore with a fluorophore near a metal nanoparticle with a subwavelength size^[3]. The fluorophores can be bound onto the metal nanoparticles that are used as the luminescent nanoparticles probes in versatile strategies^[1-6]. Up to date, MEF from metal nanostructured materials such as silver^[4-5], gold^[6], copper^[7], aluminum^[8] and zinc^[9] have been observed. In general, the interpretation of MEF is due to at least two known mechanisms^[3-9]: (1) an electric field effect and (2) coupling of excited states energies of fluorophores to surface plasmons. With the electric field effect, fluorophores in close proximity (<10 nm) to metal nanoparticles are exposed to the increased electric fields in between and around the nanoparticles, resulting in significant increases in their absorption cross section. Eventually the incident electric field and the radiative rate are increased. In the second mechanism, where the excited-state energies of fluorophores are partially transferred to surface plasmons, and then the characteristics of the excited fluorophores can be radiated by the induced plasmon together. Important factors affecting the strength of the fluorescence enhancement are the size and shape of the nanoparticles, the orientation of the fluorophore dipole moments relative to the nanoparticles surface normal, the overlap of the absorption and emission bands of the fluorophore with the plasmon band of the metal, and the radiative decay rate and quantum yield of the fluorescent molecules^[10-14]. Especially the distance between metallic surface and fluorophore is an important factor for MEF, because the fluorescence enhancement is the results from competition between the amplified incident field around metallic surface and nonradiative relaxation due to damping of the dipole oscillators by metallic surface^[15].

The lanthanide complexes display large Stokes

shifts, narrow emission bandwidths, and long emission lifetimes. Recently, growing attention has been paid for the fluorescence enhancement of lanthanide chelates, based on the MEF^[16-20], among them europium complexes were paid much attention, because europium (III) ion is a high efficient luminescence center and the complexes tend to assemble on noble-metal surface. Most studies focused on the effect of the silver island films deposited on quartz or glass slides on luminescent properties of europium complexes^[21-23], however, for biological application as the luminescent label, the metal nanostructure as an enhancer is required to be suspended in solution phase. Luminescence enhancement of europium complex (Eu(dinic)) solution with silver nanoparticles was reported by Nabika et al., concentration dependence of the enhancement was discussed in terms of silver nanoparticles taken as both an enhancer and a quencher in the system^[24]. In our previous study, the metal enhanced luminescence of europium complexes by silver nanoparticles was simply studied, and found that luminescence of the complexes was related to a stronger coupling between the surface plasmon resonance and the excited luminescence centers^[25].

In this paper, a detailed investigation of MEF from europium complex, Eu(III) DPA, where DPA is dipicolinic acid, binding to silver nanoparticles in aqueous solution was reported. The observed changes in the luminescent properties of Eu(III) DPA were discussed in terms of a stronger coupling between the surface plasmon resonance and the excited luminescence centers, re-absorption of surface plasmon resonance of silver nanoparticles, refractive index, and the ligand field around europium ion.

1 Experimental section

1.1 Materials

Silver nitrate (AgNO_3 , 99.8%), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 99%), sodium borohydride (NaBH_4 , 98%) and dipicolinic acid ($\text{C}_7\text{H}_5\text{NO}_4$, DPA) were purchased from Beijing Chemical Reagent Co., Ltd. (China). Eu_2O_3 (99.9995%) was purchased from Alfa Aesar China (Tianjin) Co., Ltd. All the reagents used were of

analytical purity and were used as received.

1.2 Preparation of samples for metal-enhanced fluorescence measurements

The synthesis of europium complex (Eu(III) $C_7H_5NO_4$, Eu(III)DPA) comprises three steps: (1) Eu_2O_3 was dissolved in concentrated nitric acid and evaporated to eliminate excessive nitric acid to obtain Eu (NO_3)₃ crystals, then added deionized water to obtain $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ Eu(NO_3)₃ solution; (2) A certain amount of the DPA was dissolved by deionized water to get $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ DPA solution; (3) Eu (NO_3)₃ solution was added into DPA solution with a molar ratio of $n_{Eu(III)}:n_{DPA}=1:1$. The solution became cloudy, and stirred vigorously until solution became clear, and cooled to room temperature, and diluted to $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ Eu(III)DPA solution for experiment. The pH value of Eu(III)DPA was 6.4. Silver nanoparticles with different sizes were prepared according to the modified methods^[26-27]. The pH value of all of silver colloids is 6.5. The samples for the optical measurements were prepared by mixing Eu (III) DPA solution and the silver colloids with keeping the measured Eu(III) ion concentration.

1.3 Apparatus and measurements

Morphologies of silver nanoparticles were observed by using of a JEOL JEM-200CX transmission electronic microscope (TEM) operated at 200 kV. Optical absorption spectra were monitored with a UV-visible spectrometer (UNICAM UV500) by using a 10 mm optical path length quartz cuvette. Luminescence measurements were recorded with a Cary Eclipse spectrofluorometer with a 90° configuration. The

luminescence spectra were collected at room temperature and under the excitation wavelength fixed at 270 nm.

2 Results and discussion

2.1 Size-dependent metal-enhanced fluorescence of silver nanoparticles

Fig.1(A) showed the UV-visible absorption spectra of four sets of silver colloids. The absorption peaks centered at 398, 400, 436 and 446 nm, respectively. The TEM images of the corresponding silver nanoparticles were shown in Fig.1 (B). The mean diameter of silver nanoparticles was 5, 14, 35 and 46 nm, respectively. The absorption peak was red-shifted with increasing of silver nanoparticles size, which attributed to the surface plasma resonance in the silver nanoparticles^[26].

Fig.2 showed the UV-visible absorption spectra of $3 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ Eu (III) DPA solution containing different amounts of silver colloids ($d=46 \text{ nm}$). The amount of silver colloid from curve a to h in Fig.2 was 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mL. The insert was absorption spectrum of the pure Eu(III)DPA solution. As can be seen from Fig.2, there were two absorption bands around at 270 nm and 446 nm, which was assigned to the $\pi-\pi^*$ of DPA and the surface plasma resonance of silver nanoparticles, respectively. With the increase of the amount of silver colloid, intensities of both of absorption bands increased.

Fig.3 (A) showed the emission spectrum of DPA solution ($10^{-4} \text{ mol} \cdot \text{L}^{-1}$) with broad emission band centered at around 448 nm and the excitation

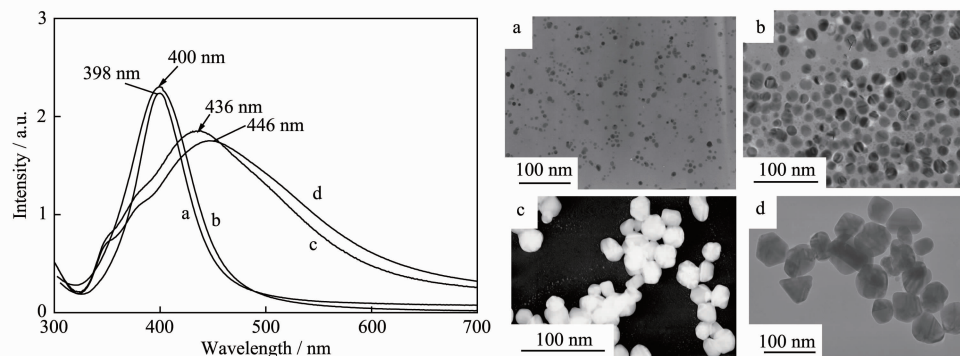


Fig.1 (A) Absorption spectra and (B) TEM images of the corresponding silver nanoparticles, the mean diameter of silver nanoparticles from image (a) to (d) was 5, 14, 35 and 46 nm, respectively

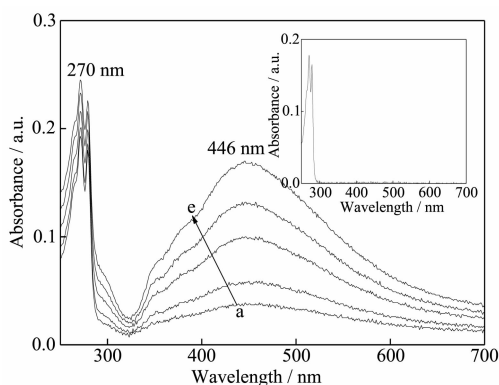


Fig.2 Absorption spectra of Eu(III)DPA solution containing different amounts of silver colloids ($d=46$ nm), the amounts of silver colloid from curves a to h were 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mL, Inset is absorption spectrum of the pure Eu(III)DPA solution

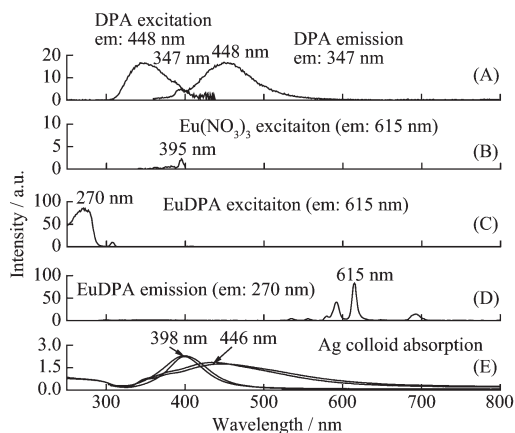


Fig.3 Emission spectrum of DPA solution (10^{-4} mol·L $^{-1}$) (A), excitation spectrum of Eu $^{3+}$ solution (10^{-2} mol·L $^{-1}$) (B), excitation (C) and emission spectrum (D) of Eu(III)DPA solution (10^{-4} mol·L $^{-1}$), and optical absorption of silver colloids (E)

maximum at 347 nm. The excitation spectrum of Eu(NO $_3$) $_3$ (10^{-2} mol·L $^{-1}$, Fig.3(B)) was obtained by monitoring $^5D_0 \rightarrow ^7F_2$ transition at 615 nm and the most intense excitation band was $^7F_0 \rightarrow ^5L_6$ transition at 395 nm. It can be clearly seen that there was an overlap between the emission band of DPA and the excitation band of Eu(NO $_3$) $_3$ in the wavelength region of 350 nm to 400 nm, which indicated Frster energy transfer between DPA and Eu(III). The excitation spectrum of Eu(III)DPA complex (10^{-4} mol·L $^{-1}$, Fig.3(C)) was also obtained by monitoring $^5D_0 \rightarrow ^7F_2$ transition at 615 nm, in which an strong peak at around 270 nm and almost no peak at around 390~400 nm. The peak observed at

270 nm was thought to be attributable to the excitation of DPA. Several sharp bands characteristic of the f-f transitions of Eu(III)DPA were observed in the emission spectrum of Eu(III)DPA solution (10^{-4} mol·L $^{-1}$, Fig.3(D)) with the excitation at 270 nm.

Effects of the silver nanoparticles ($d=46$ nm) with different amounts of silver colloids on the emission spectra of Eu(III)DPA solution (excited by 270 nm) were investigated in Fig.4. The amount of silver colloids from curve a to f is 0, 0.05, 0.1, 0.6, 0.8, and 2.0 mL. Five emission peaks centered at 556, 592, 615, 649, and 693 nm, assigned to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions, respectively, were observed. Two strong emission bands, separately corresponding to electric dipole $^5D_0 \rightarrow ^7F_2$ transition at 615 nm and magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition at 592 nm, were both enhanced by silver nanoparticles with the low concentration, while the emission wavelength remained unchanged. With the increase of the amount of silver colloid, the intensities of both bands increased initially and then decreased after a maximum.

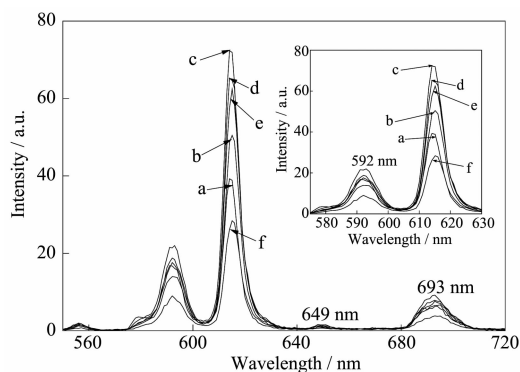


Fig.4 Emission spectra of Eu(III)DPA solution ($\lambda_{ex}=270$ nm) with different amounts of silver colloids ($d=46$ nm), Selective enlargement image is inserted, Amount of silver colloids from curves a to f were 0, 0.05, 0.1, 0.6, 0.8, and 2.0 mL

The amount of silver colloids with different sizes dependence on the enhancement efficiency of Eu(III)DPA was illustrated in Fig.5, in which the enhancement efficiency was the integral intensity ratio of Eu(III)DPA solution containing silver colloid to Eu(III)DPA solution at $^5D_0 \rightarrow ^7F_1$ (Fig.5(A)) and $^5D_0 \rightarrow ^7F_2$ (Fig.5 (B)) transitions. Seen from Fig.5, the enhancement

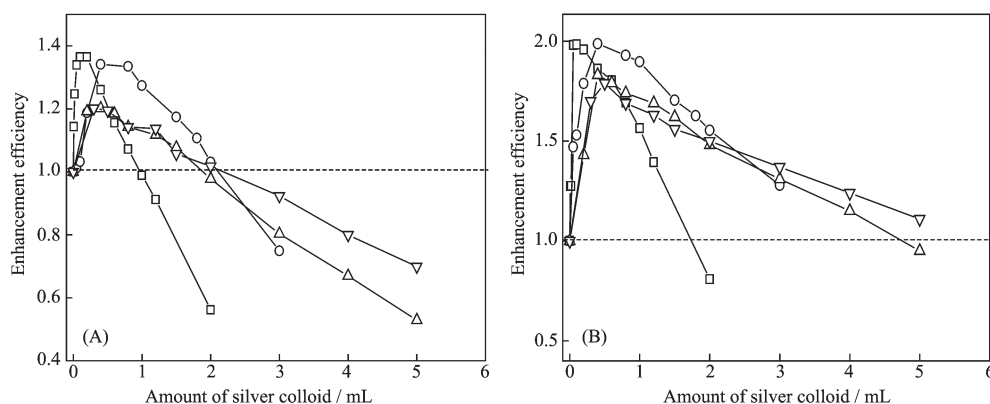


Fig.5 Enhancement efficiency for Eu(III)DPA solution containing silver colloids with different sizes at $^5D_0 \rightarrow ^7F_1$ (A) and $^5D_0 \rightarrow ^7F_2$ (B) transitions: particle with $d=5$ nm (▽), 14 nm (☆), 35 nm (○), and 46 nm (□)

efficiency was strongly affected by the size and concentration of the silver nanoparticles. For $^5D_0 \rightarrow ^7F_2$, the emission was enhanced in a large range of silver nanopartilces concentrations to four sets of silver nanoparticles, the maximum of enhancement factor was about 1.99 at 0.1 mL silver colloid with the diameter of 46 nm. For $^5D_0 \rightarrow ^7F_1$, the enhancement was only observed at a small range of silver colloid amount, and the maximum enhancement factor was 1.36 at 0.1 mL silver colloid with the diameter of 46 nm. It was indicated that the enhancement of the electric dipole transition was much higher than that of magnetic dipole transition. Similar phenomenon was reported by Nabika^[22-23], and attributed to the modifications of the ligand field and the refractive index around europium ions arising from the interaction with silver nanoparticles, which affect the hyper-sensitive transition. The large nanoparticles resulted in the high enhancement efficiency and the low amount at which the enhancement efficiency reaches the maximum. Theoretical studies showed that larger metal nanoparticles have better fluorescence enhancement effects compared with smaller ones^[28]. This finding was also in agreement with the conclusion made by Ref.14 and 29 that the MEF of a bigger gold nanorod or nanoparticles was stronger than that of a smaller one.

It is well accepted that the luminescent properties of luminescent materials located near metal nanoparticles are affected by the near-field electro-dynamical environment, which cause enhancement or quenching of the luminescence depending on

the distance between the molecule and the metal surface^[2,8-9,13]. Non-radiative energy transfer to surface plasmon resonances in the metal takes place when the distance between fluorescent molecules and metal surface is very short. Due to surface plasmon resonances of metal nanoparticles electromagnetic-field enhancement occurs only at proper distance^[3-6,14]. With increasing of amount of silver nanoparticles, more and more Eu(III)DPA were localized or close to silver nanoparticles until saturated, so the interaction distance between silver nanoparticles and Eu(III)DPA became shorted. The emission intensity was quenched due to resonance energy transfer from the molecule to the metal surface^[13,17,20]. Otherwise, further increasing of silver nanoparticles amount, re-absorption of surface plasmon resonance of silver nanoparticles was dominant, so intensity gradually decreased. On the other hand, seen from Fig.5, the concentration dependencies of emission intensities for the electric dipole $^5D_0 \rightarrow ^7F_2$ transition and magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition were quite different, so we proposed the enhancement was related to a stronger coupling between the surface plasmon resonance and the excited luminescence centers, in which results the fact that the component of electric dipole resonance in the surface plasma of metallic nanoparticles was much stronger than that of magnetic dipole resonance, the enhancement of electric dipole transition should be stronger than that of magnetic $^5D_0 \rightarrow ^7F_1$ transition. As shown in Fig.3(E), the absorption of silver colloid covered over wide wavelength region from 300 to 600

nm, which was the similar region to the resonant energy level between DPA and Eu(III) ion. It was deduced that the observed enhancement seemed to be the results from delicate balance of the local electromagnetic field enhancement and re-absorption of surface plasmon resonance^[24].

The $^5D_0 \rightarrow ^7F_2$ transition is the hyper-sensitive to the first coordinative environment around europium ion. The fluorescence intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transitions indicated the degree of asymmetry in the vicinity of europium ions and Eu-O covalency^[29-30], and is the so-called asymmetry ratio, AS. The variation in the AS value indicated the modifications of the ligand field and the refractive index around europium ions^[29-30]. Fig.6 showed AS dependence of amount of silver nanoparticles with different sizes. It is notable that the trend of the AS change is different to silver nanoparticles with different sizes. The AS value increased monotonically with the increase of the small sizes (5 nm, 14 nm) silver nanoparticles amounts, while the AS first increased and then decreased with the increase of large sizes (35 nm, 46 nm) silver nanoparticles amounts. These differences arise from the different local fields owing to the induced surface plasmons resonance of silver nanoparticles. The change in the AS values indicated the ligand field and the refractive index around europium ions were altered due to the presence of the silver nanoparticles. The ligand field distortion is explained on the basis of interaction between silver nanoparticles and DPA results in the changes in the coordination structure

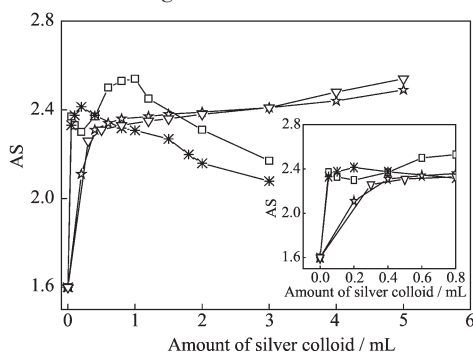


Fig.6 AS dependence of amount of silver nanoparticles with different sizes, Selective enlargement image is inserted, Sizes of silver nanoparticles are 5 nm (∇), 14 nm (\star), 35 nm ($*$), and 46 nm (\square)

around europium ion. The modification of the local refractive index around europium is regarded as the result of the local field effect, which gives the refractive index dependence of the electric dipole transition rate.

2.2 Concentration of Eu(III)DPA solution-dependent metal-enhanced fluorescence of silver nanoparticles

Fig.7 showed the UV-visible absorption spectra of $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (Fig.7(A)) and $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ (Fig.7(B)) Eu(III)DPA solutions containing silver colloids. Upon adding silver nanoparticles into the above Eu(III)DPA solutions, the color of solutions immediately changed to pinkish red and deepened with the increase of Eu(III)DPA solution concentration, accompanying the appearance of a new absorption at longer wavelength region, indicated the interaction between silver nanoparticles and Eu(III)DPA complex to form nanoparticles aggregates in the solution^[26]. The higher concentration solution the greater nanoparticles aggregate. The effect of the Eu(III)DPA complex solution concentration on silver nanoparticles was attributed to the results of the intermolecular hydrogen bonding ability of carboxylic acid, namely, DPA. The DPA is polycarboxylic acids and its dissociation constant is affected by the pH value of solution. With increasing of the Eu(III)DPA solution concentration from $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ to $10^{-2} \text{ mol} \cdot \text{L}^{-1}$, the pH value decrease, and Eu(III)DPA complexes are partially ionized, and carboxylic acid groups not only bind to the surface of silver nanoparticles but

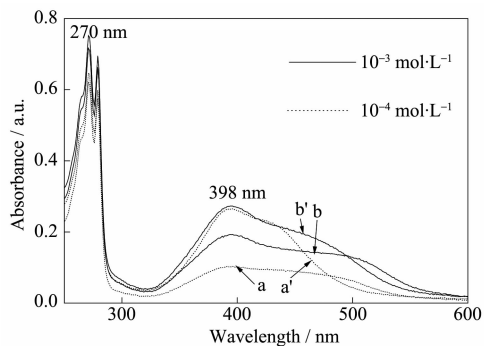


Fig.7 Absorption spectra of Eu(III)DPA solution with concentrations of $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (A) and $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ (B) containing Ag nanoparticles ($d=5 \text{ nm}$), the amounts of silver colloid were 0.5 mL (a, b), and 1.0 mL (a', b')

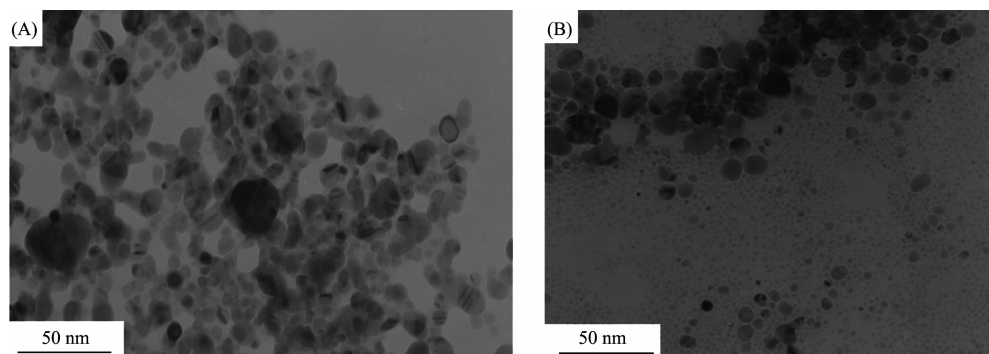


Fig.8 TEM images of $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (A) and $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ (B) Eu(III)DPA solutions containing silver nanoparticles ($d=5 \text{ nm}$)

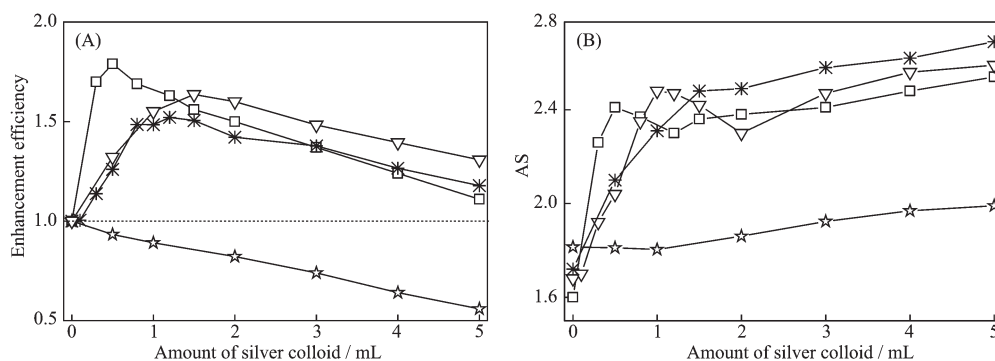


Fig.9 Enhancement efficiency of at ${}^5D_0 \rightarrow {}^7F_2$ transition (A) and AS (B) for Eu(III)DPA solutions with concentrations of $3.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ (\square), $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ($*$), $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (∇), and $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (\star)

also further interaction between Eu(III)DPA complexes through intermolecular bonding to yield nanoparticles assemblies. The representative TEM images of Eu(III)DPA solutions containing silver nanoparticles ($d=5 \text{ nm}$) were shown in Fig.8. Compared with Fig.1 (B), silver nanoparticles aggregates were observed in both of solutions and the aggregates are larger in $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ solution than that of in $10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

The enhancement efficiencies of ${}^5D_0 \rightarrow {}^7F_2$ transition (Fig.9(A)) and AS (Fig.9(B)) of Eu(III)DPA solutions with different concentrations were illustrated in Fig.9. Seen from Fig.9, the emissions of ${}^5D_0 \rightarrow {}^7F_2$ transition were enhanced in a large range of silver colloid concentrations when the concentration of Eu(III)DPA solution was less $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, and the maximum enhancement factor decreased with the increase of Eu(III)DPA solution concentration. Otherwise, the emission of ${}^5D_0 \rightarrow {}^7F_2$ transition decreased monotonically with the particle concentration in the $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ Eu(III)DPA solution. It was deduced from Fig.9 that the nonradiative rate was increased due to the change of effective distance between the metallic surface and Eu(III)DPA molecular and the

inhibition of surface plasmons resonance of silver nanoparticles aggregates. The tendency in AS values with the silver nanoparticles concentrations and Eu(III)DPA solutions indicated that the increase in the distortion of the ligand field arising from the interaction with silver nanoparticles during the aggregate formation in the high concentration Eu(III)DPA solutions. In this research, we noticed that when the pH value range of $3.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ Eu(III)DPA solution was 4~7, the enhanced luminescence was observed, while the pH value is more than 4, the luminescence was quenched. When the pH value was more than 7, the luminescence was little change. It was indicated that the effects of silver colloids on the luminescent properties of europium complex were closely related to the state of a combination of both, that is mainly depends on the distance between them, which affected to the coupling between the surface plasmon resonance and the excited luminescence centers.

3 Conclusions

A detailed study of the effects of silver

nanoparticles on the luminescent properties of the europium complex (Eu(III)C₇H₅NO₄, Eu(III)DPA), where DPA is dipicolinic acid, in the aqueous solution system was reported. The emission intensity of the Eu(III)DPA solution initially increased with increasing of the amount of silver colloids and then decreased. The large silver nanoparticles resulted in the high enhancement efficiency and the low amount at which the enhancement efficiency reaches the maximum. For $^5D_0 \rightarrow ^7F_2$, the emission was enhanced in a large range of silver colloid concentrations, and for $^5D_0 \rightarrow ^7F_1$, the enhancement was only observed at a small range of silver colloid amount. The emission intensity of high Eu(III)DPA solution concentration was quenched by silver nanoparticles. The observed silver nanoparticles dependences of the luminescent intensity were regarded as the result of a stronger coupling between the surface plasmon resonance and the excited luminescence centers and re-absorption of surface plasmon resonance of silver nanoparticles. Meanwhile, the asymmetric ratio of the europium luminescence affected by silver nanoparticles was discussed in terms of the local electromagnetic field enhancement, refractive index, and the ligand field around europium ion.

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