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Resonance light scattering properties of Eu^{3+} in gold colloid

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Abstract

Gold colloidal containing rare-earth ions Eu^{3+} were prepared at room temperature. Fluorescence spectra and resonance light scattering (RLS) spectra of Eu^{3+} ions and gold colloid containing Eu^{3+} were measured. For solution containing Eu^{3+}, RLS features show two peaks at the edges of the visible light wavelength region. The short wavelength peak takes place at about 400 nm and the longer wavelength peak is the corresponding 1/2 fraction frequency RLS peak, which takes place at about 780 nm. When gold colloids were added to the solution containing Eu^{3+}, both these two RLS peaks were enhanced. We believe that the energies, which are absorbed by the surface plasmon resonance in the gold nanoparticles, are efficiently transferred into the Eu^{3+} ions to cause the increased scattering.
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1. Introduction

Rare-earth ions such as Eu^{3+} and Dy^{3+} in different host material are of current interest because of their special electronic and optical properties and potential applications [1–10]. In the paper of Dejneka et al. [2], red, green, blue and novel UV fluorescence have been observed in Eu^{3+}-doped fluoride glasses. The effect of increasing Eu^{3+} concentration on emission was found to decrease blue emission and increase the green and red via nonradiative dipole–quadrupole and dipole–dipole ion pair transitions. Rambabu et al. [3] have reported the fluorescence properties of a new series of Eu^{3+}-doped powder phosphors based on GdOBr, LaOBr and YOBr. The relative fluorescence intensity ratios for the different measured emission levels were also evaluated in order to examine the host matrix compositional effects on the fluorescence behaviours. In the letter of Nogami et al. [4], Eu^{3+}-doped SnO_2–SiO_2 glasses were prepared using a sol–gel method, where nanosized SnO_2 crystals of ∼8 nm in diameter were precipitated to dope the Eu^{3+} ions. In the paper of Magyar et al. [5], chelation of rare-earth (RE) ions is investigated as a means of enhancing the optical properties of RE-doped silica sol–gels. Two chelating agents 2,6-pyridinedicarboxylic acid (PDC) and 3-pyridinepropionic acid (PPA) and two different synthesis techniques are studied. Eu (PDC) gels exhibit intense $^5D_0$–$^7F_2$ fluorescence in the red under UV excitation and long fluorescence lifetimes compared to Eu (PPA) gels and to gels without a chelating agent.

The physical and chemical characteristics of colloid gold appear most attractive because of their special electromagnetic modes such as surface modes and local field. Surface plasmons are collective electromagnetic oscillations at metallic surfaces. It is widely accepted that for optical processes the primary role of the roughness in metals or the small size of noble metal particles is to enhance the local optical fields via localized plasmon resonance, and thus improve the efficiency of light absorption and emission [11–13]. Hayakawa et al. [8] have described the increase of europium ion fluorescence owing to resonant plasma oscillation of silver particles in silica glass, which were precipitated by annealing in a reducing atmosphere sol–gel-derived SiO_2 glass containing

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Ag^+ and Eu^{3+} ions. They have come to the conclusion that the most probable mechanism for the fluorescence increase is a local field enhancement around Eu^{3+} ions, due to the induced surface plasmon resonance of Ag particles. Nogami et al. [4] have reported that when excited at the energy corresponding to the absorption edge of the SnO_2 nanocrystals, the SnO_2-doped glass exhibits fluorescence intensities of the Eu^{3+} ions higher than 150 times that of the glass without nanocrystals. The energies, which are absorbed by the quantum-dot effect in the nanosized crystals, are efficiently transferred into the Eu^{3+} ions to cause the high emission.

If a solid particle is illuminated by electromagnetic wave, electric charges in the obstacle will be set into oscillatory motion. Accelerated electric charges radiate electromagnetic energy in all directions, this secondary radiation is called scattering. If the wavelength of the incident beam is close to that of the absorption band of the molecular particles, Rayleigh scattering will deviate from the ordinary law and the intensity of some wavelengths will rapidly increase. This phenomenon is called resonance light scattering (RLS) [14–16]. In recent years, RLS as a new analytical technique has been applied to the study and determination of some biological macromolecules, ion-association complexes, trace amounts of metals, non-metals and so on [16–20]. In this paper, we study on the resonance light scattering properties of gold colloid containing Eu^{3+}. Two RLS peaks are observed at 400 and 780 nm, respectively. Enhancement of these scattering peaks has also been observed by the addition of gold colloids. Furthermore, we discuss in detail the mechanisms of the enhanced RLS from Eu^{3+} in gold colloids.

2. Experimental

Europium oxide Eu_2O_3 (0.03 g) was dissolved in H_2O (25 ml, including 20% HNO_3). This synthesis was conducted under an ultrasonication at room temperature. The resultant solution was transparent and has no color. Gold colloid nanoparticles were prepared via electrochemical method [21,22]. The transmission electron microscopic (TEM) images are obtained by using a JEOL JEM-200CX TEM, the gold nanoparticles with mean diameter 15 nm have been observed, as shown in Fig. 1. The color of the resultant solution was red. At last, amounts of gold colloid were added to the solution containing Eu^{3+} with gentle mixing. Then the resultant solution turns to light pink.

3. Results and discussion

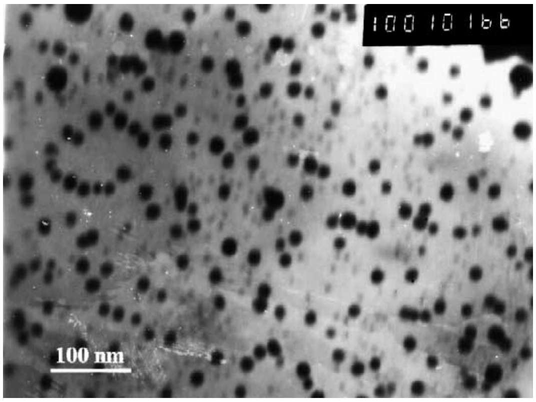

Fig. 1. TEM image of gold colloidal nanospheres.

The fluorescence spectra are recorded on a Perkin Elmer LS 55 spectrophotofluorometer. It is known that the fluorescence spectra of Eu^{3+} consist of a series of resolved bands peaking at 570–630 nm, which are assigned to $^5D_0 \rightarrow {}^7F_j$ ($j = 0, 1, 2, 3, 4$) transitions. Among the $^5D_0 \rightarrow {}^7F_j$ transitions, the $^5D_0 \rightarrow {}^7F_2$ band at 620 nm is an electric dipole transition and sensitive to chemical bonds in the vicinity of Eu^{3+} ions [4]. So the fluorescence excitation spectra are studied in order to find the sensitive excitation frequency. The excitation spectrum in Fig. 2 is the scanning excited wavelength from 200 to 600 nm when the detection wavelength was located at 620 nm. The experimental results in Fig. 2 show that the fluorescence at 620 nm is sensitive to the excitation at 395 nm. It is important to note that when amount of gold colloid were added to the solution containing Eu^{3+}, the corresponding excitation peaks increase, as shown in Fig. 2.

Solution containing only Eu^{3+} and solution containing both gold nanoparticles and Eu^{3+} are excited at 395 nm. The corresponding fluorescence emission spectra are compared in Fig. 3. For solution containing only Eu^{3+}, five emission peaks fixed at 535, 555, 590, 620 and 695 nm display. We believe that these fluorescence peaks are resulted from $^5D_1 \rightarrow {}^7F_1$, $^5D_1 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ band transitions of the Eu^{3+}, respectively [2,3]. Whereas when amount of gold colloid were added to the solution containing Eu^{3+}, most of these fluorescence emission peaks increase. We believe that these enhanced fluorescence are due to the local

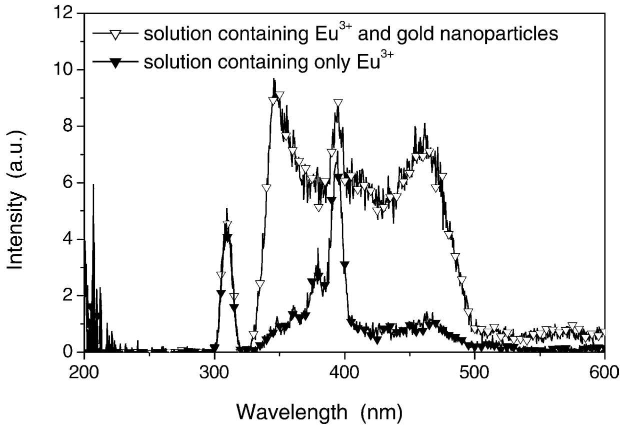

Fig. 2. Fluorescence excitation spectra of solution containing only Eu^{3+} and solution containing both gold nanoparticles and Eu^{3+} (detection wavelength is 620 nm).

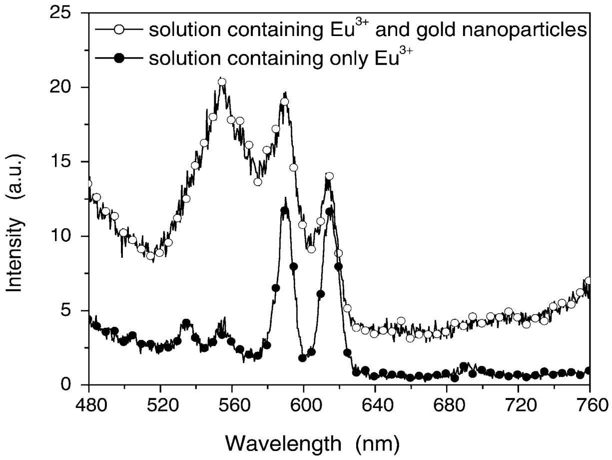

Fig. 3. Fluorescence emission spectra of solution containing only Eu^{3+} and solution containing both gold nanoparticles and Eu^{3+} (exciting at 395 nm).

field enhancement around Eu^{3+} ions owing to the induced surface plasmon resonance of gold nanoparticles and energy transfer from gold nanoparticles to Eu^{3+} ions.

The RLS spectrum is the spectrum that showed the excited and emission wavelengths synchronously in the form of $\Delta\lambda = 0$ ($\lambda_{ex} = \lambda_{em}$) [16]. Fixed the detection wavelength equal to the excitation wavelength, we get the intensity of scattering light. Compared the relative intensity of the scattering peaks with different excited wavelengths, we find that the resonance light scattering are intense from 380 to 480 nm and the strongest peak is at about 400 nm. Furthermore, the corresponding 1/2 fraction frequency RLS peak at 780 nm is also observed, as shown in Fig. 4. This nonlinear scattering phenomenon could be illustrated from the pump effect and theory of quanta optics [16,23]. It is important to note that when amount of gold colloid were added to the solution containing Eu^{3+}, both these two RLS peaks increase, as shown in Fig. 4. The solution containing both gold colloid and Eu^{3+} exhibits RLS intensities higher than 1.5 times at 400 nm and 7.5 times at 780 nm that of solution containing only Eu^{3+} ions. It is interesting to note that the scattering enhancement at 780 nm is more intensive than that at 400 nm. This result indicates that the increase of 1/2 fraction frequency RLS peak is more sensitive to the addition of gold nanoparticles.

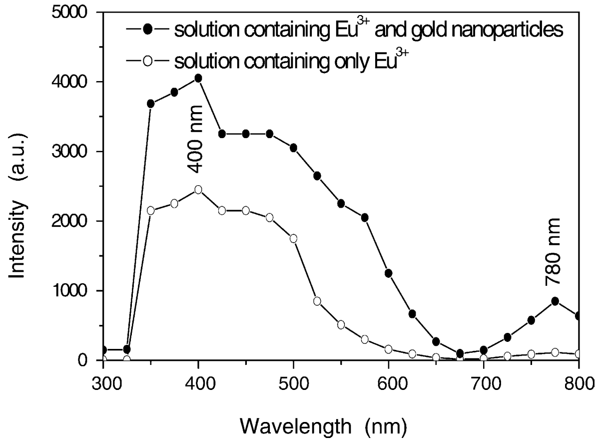

Fig. 4. Resonance light scattering spectra of solution containing only Eu^{3+} and solution containing both gold nanoparticles and Eu^{3+}.

It is well known that the scattering is essentially the reradiation from the accelerated electric charges. When the incident beam is close to that of the absorption band of the molecular particles, the RLS will takes place. The excitation peak fixed at 395 nm in Fig. 2 shows that the fluorescence from Eu^{3+} is sensitive to the excitation at 395 nm. Furthermore, in Ref. [4], the absorption band due to the f–f transitions of the Eu^{3+} ions was observed at 395 nm. So we believe that this resonance scattering peak fixed at about 400 nm in Fig. 4 is attributed to the coupling between the excitation light and the absorption band of Eu^{3+}.

When gold colloids were added to the solution containing Eu^{3+}, the environment of Eu^{3+} has changed and the gold nanoparticles play an important role. Excitation of the gold nanoparticles at 400 nm leads to excitation of the surface plasmon coherent electronic motion. According to the theoretical research of the photo-induced luminescence [24], both the incoming and outgoing fields are propose to be enhanced via coupling to the local plasmon resonance. The dependence of the Eu^{3+} radiation intensity on the gold nanoparticles suggests the energy transfer from the nanoparticles to Eu^{3+}. When Eu^{3+} ions in the solution adsorb on the surface of gold nanoparticles, the energy of collective electromagnetic oscillations at gold surfaces will transfer from gold nanoparticles to Eu^{3+} ions [25]. So the enhanced oscillatory of the electric charges results in the enhanced secondary radiation and the increased scattering.

4. Conclusion

Fluorescence and RLS characters of solution containing Eu^{3+} have been studied at room temperature. Two resonance light scattering peaks are observed at 400 and 780 nm, respectively. Both these two scattering peaks are enhanced when amount of gold colloid are added to the solution containing Eu^{3+}. We believe that the scattering peak fixed at about 400 nm is attributed to the coupling between the excitation light and the absorption band of Eu^{3+}. Furthermore, the enhancement of the scattering is due to the energy transfer from the local field in gold nanoparticles to Eu^{3+} ions.

References

[1] P. Srivastava, S.B. Rai, D.K. Rai, Spectrochim. Acta Part A 59 (2003) 3303.

[2] M. Dejneka, E. Snitzer, R.E. Riman, J. Luminescence 65 (1995) 227.

[3] U. Rambabu, P.K. Khanna, I.C. Rao, S. Buddhudu, Mater. Lett. 34 (1998) 269.

[4] M. Nogami, T. Enomoto, T. Hayakawa, J. Luminescence 97 (2002) 147.

[5] A.P. Magyar, A.J. Silversmith, K.S. Brewer, D.M. Boye, J. Luminescence 108 (2004) 49.
[6] S.T. Selvan, T. Hayakawa, M. Nogami, J. Non-Cryst. Solids 291 (2001) 137.
[7] M. Nogami, T. Yamazaki, Y. Abe, J. Luminescence 78 (1998) 63.
[8] T. Hayakawa, S.T. Selvan, M. Nogami, J. Non-Cryst. Solids 259 (1999) 16.
[9] G. Jose, V. Thomas, C. Joseph, M.A. Ittyachen, N.V. Unnikrishnan, Mater. Lett. 57 (2003) 1051.
[10] K.R. Reddy, K. Annapurna, S. Buddhudu, Mater. Res. Bull. 31 (1996) 1355.
[11] G.T. Boyd, Th. Rasing, J.R.R. Leite, Y.R. Shen, Phys. Rev. B 30 (1984) 519.
[12] J. Zhu, Y.C. Wang, Y.M. Lu, Colloid. Surf. A 232 (2004) 155.
[13] J. Zhu, Y.C. Wang, S.N. Yan, Chin. Phys. Lett. 21 (2004) 559.
[14] J. Aglister, I.Z. Steinberg, J. Chem. Phys. 78 (1983) 5358.
[15] C.F. Bohren, Absorption and Scattering of Light by Small Particles, Wiley-Interscience, New York, 1983, p. 371.
[16] Z.L. Jiang, S.P. Liu, S. Chen, Spectrochim. Acta Part A 58 (2002) 3121.
[17] X.L. Liu, H. Yuan, D.W. Pang, R.X. Cai, Spectrochim. Acta Part A 60 (2004) 385.
[18] R.C. Johnson, J.T. Li, J.T. Hupp, G.C. Schatz, Chem. Phys. Lett. 356 (2002) 534.
[19] Z.L. Jiang, Q.Y. Liu, S.P. Liu, Spectrochim. Acta Part A 58 (2002) 2759.
[20] J. Zhu, Y.C. Wang, L.Q. Huang, Y.M. Lu, Phys. Lett. A 323 (2004) 455.
[21] Y.Y. Yu, S.S. Chang, C.L. Lee, C.R.C. Wang, J. Phys. Chem. B 101 (1997) 6661.
[22] J. Zhu, Y.C. Wang, Plasma Sci. Technol. 5 (2003) 1835.
[23] A. Hellemans, Science 284 (1999) 24.
[24] G.T. Boyd, Z.H. Yu, Y.R. Shen, Phys. Rev. B 33 (1986) 7923.
[25] O.L. Malta, M.A. Couto dos Santos, Chem. Phys. Lett. 174 (1990) 13.