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Europium(III) Complexes/Silica Hybrid Nanospheres Synthesized in Microemulsion

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$Eu(DBM)_3Phen$/silica nanospheres with a uniform diameter of ~40 nm and the characteristic fluorescence of Eu^{3+} ions have been synthesized by a microemulsion method. SEM and TEM analysis indicate that the hybrid nanospheres are core/shell structures with fine spherical surfaces and that $Eu(DBM)_3Phen$ has been successfully enveloped in the SiO_2 spheres as chromophore cores. IR absorption spectra and photoluminescence spectra suggest that the hybrid nanoparticles are promising materials for bioassay.

Keywords: $Eu(DBM)_3Phen$/Silica, Nanospheres, Microemulsion, Photoluminescence.

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1. INTRODUCTION

Colloidal silica spheres are interesting materials not only for building photonic crystals but also for mini optical functional devices. Some significant works have been reported on the two topics.[1–6] One important functional improvement is the implanting of chromophores into the colloidal silica spheres in order to study the effect of photonic band structure on the spontaneous emission and to develop biosensors or biological labels.[7–9] Lanthanide ions with characteristic sharp band emissions have been used as implanted chromophores in the silica nanospheres for biological purposes.[10–12] The silica layer provides several advantages for bioassay applications. First, the silica layer can isolate the cores from harsher conditions presented by biological media and increase the photostability and luminescent efficiency of the implanted chromophores.[8,12,13] Second, compared to a single lanthanide chelate molecule, the optical detection sensitivity of a hybrid nanosphere is much greater due to a lot of lanthanide chelate molecules in it.[8] Additionally, silica has high biocompatibility and an easily modified surface, to which we can link different biologically active functional groups.

Zhao et al. synthesized monodisperse and 300-nm spherical $Eu(DBM)_3Phen$-embedded silica spheres with a modified Stöber method[9] and modified the spontaneous emission of the europium complex by dispersing the silica spheres in different dielectric polymers,[14] making the Eu^{3+} ions promising probe for the study of photonic crystals. Yuan et al. have reported on the synthesis of silica nanospheres containing lanthanide-based luminescence probes in microemulsion and their applications to time-resolved luminescence bioassays.[12,13] In their experiments, the organic chromophores coordinated with lanthanide ions are mainly tetradentate β-diketone.

In this report, we used a microemulsion to introduce $Eu(DBM)_3Phen$, a kind of excellent and easily fabricated photoluminescent material, into silica nanospheres. We present the microemulsion as an effective method to incorporate excellent photoluminescent materials in silica nanospheres with potential application in bioassays and biolabeling.

2. EXPERIMENTAL DETAILS

The $Eu(DBM)_3Phen$/silica nanospheres were synthesized by a two step process. First, the $Eu(DBM)_3Phen$ complex was prepared as follows. 0.003 mol of the negatively charged dibenzoyl unit and 0.001 mol of 1,10-phenanthroline were dissolved in 40 mL ethanol under stirring. Then, 1 mmol of $EuCl_3$ ethanol solution was added, and the pH of the solution was adjusted to 6–7 with absolute sodium ethylate. The solution was stirred for 3–4 hours at constant temperature to obtain

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the stable water-free octa-coordinated form. The precipitate was washed with acetone and absolute ethanol and recrystallized with acetone.

Second, the silica was formed in a water/oil (W/O) microemulsion. A microemulsion containing 30 mg pure complex and 200 μL TEOS were dispersed into a solution of Triton X-100, octanol, cyclohexane, water (4:2:2:1, v/v) under stirring. Another W/O microemulsion containing Triton X-100, octanol, cyclohexane, (4:2:2, v/v) and 200 μL concentrated ammonium hydroxide (25%) was added with vigorous stirring. After the hydrolysis and polycondensation of TEOS for several hours, 10 μL APS was added into the solution, and the mixture was stirred over night. The product was obtained by centrifuging and rinsing thoroughly with acetone, ethanol, and water.

The size and morphology of the nanoparticles were characterized by TEM (JEM, 2000EX 200KV) and SEM (XL 30 ESEM FEG, FEI Company). IR absorption spectra with the range of 4000–500 cm^{-1} in KBr suspensions were registered by a Bio-Rad FTIR spectrometer. Room-temperature emission spectra were performed with a Hitachi F-4500 fluorescence spectrometer.

3. RESULTS AND DISCUSSION

The water/oil microemulsion is a simple and efficient method for preparing of core/shell nanoparticles. The spherical silica-coated fluorescent nanoparticles modified with amino groups were obtained by simultaneous hydrolysis and copolymerization reactions of TEOS and APS in a W/O microemulsion containing an aqueous solution of $Eu(DBM)_3Phen$, surfactant Triton X-100, cosurfactant octanol, and oil phase cyclohexane. Figures 1 and 2

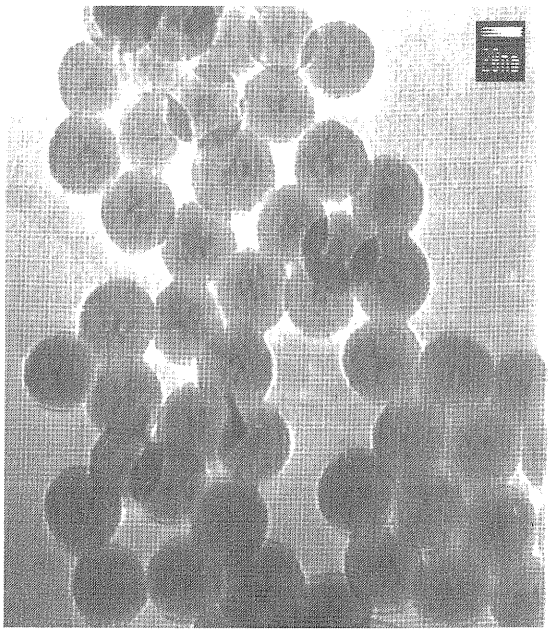

Fig. 1. TEM of europium complex/silica hybrid nanoparticles.

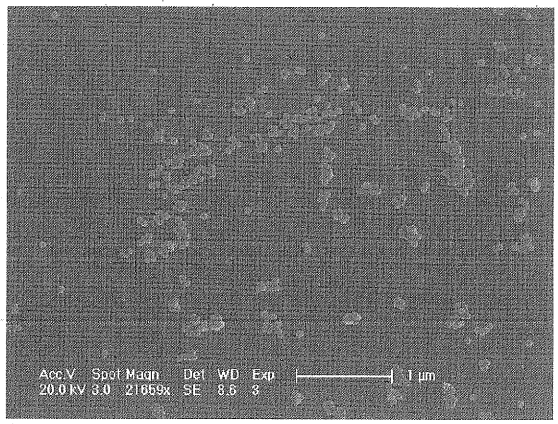

Fig. 2. SEM of europium complex/silica hybrid nanoparticles.

show the TEM and SEM images of $Eu(DBM)_3Phen$/silica nanospheres, respectively. The dark dots embedded inside the silica network are visible in the TEM image. These dark dots originate from europium chelate molecular aggregates in the water pools of the microemulsion during the formation of the silica network. The images show that the silica-coated hybrid nanoparticles have a particle size nearly 40 nm, regular spherical shape, and good dispersity. The silica shell thickness can be varied with well-controlled reagent concentration, reaction time, and W/O ratio.[8, 12, 15, 16]

Figure 3 shows the infrared absorption spectra of europium complex and nanospheres. The IR spectrum of the $Eu(DBM)_3Phen$ presents a complex pattern of peaks. The peak around 3065 cm^{-1} is based on the CH=CH stretching vibrational mode corresponding to the phenyl unites of the derivative. The peaks in the range of 1600–1400 cm^{-1} are attributed to the C=O, C=C, and C=N stretching modes of β-diketonate and phenanthroline ligands. In regard to the silica-coated nanoparticles, the typical peak intensities of the organic ligands were weaker than that of

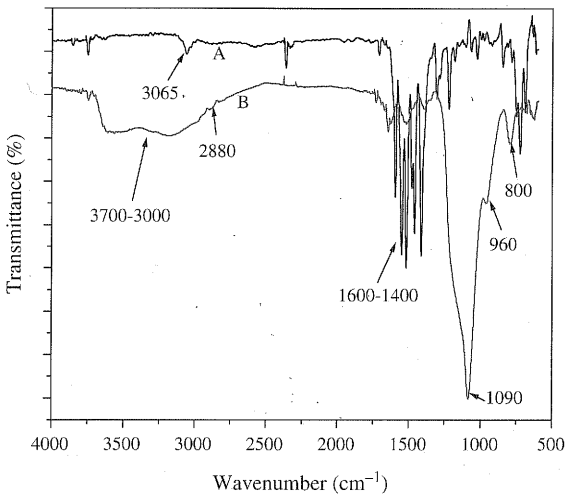

Fig. 3. Infrared absorption spectra of (A) europium complex and (B) europium complex/silica hybrid nanoparticles.

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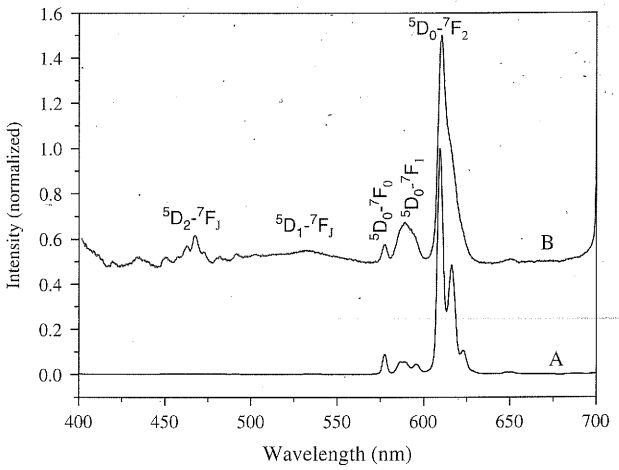

Fig. 4. Emission spectra of (A) europium complex and (B) europium complex/silica hybrid nanoparticles.

the strong absorption peak at around 1090 cm^{-1}, which is attributed to Si—O—Si asymmetrical stretching vibration. The symmetric stretching of Si—O—Si at 800 cm^{-1} and symmetric stretching of Si—OH at 960 cm^{-1} also appear in the spectrum of silica-coated nanoparticles. The CH=CH stretching vibrational mode in the silica-coated nanoparticles is shifted to 2880 cm^{-1}, which indicates there are some interactions between the europium complex and the silica shell.[13] The absorption bands in the region of 3700–3000 cm^{-1} are based on the stretching vibration of amino groups around the silica shell, but hydroxy groups cannot be eliminated because of intrinsic hydrolyzed mechanism of TEOS and APS. The presence of characteristic bands of the $Eu(DBM)_3Phen$ complex suggests that the europium complex is incorporated in the silica spheres and free amino groups are introduced to the surface of silica sphere.

Figure 4 shows the emission spectra under 355-nm excitation that correspond to the absorption of the β-diketonnato ligands. The strongest emission at 611 nm is due to the force electric dipole transition ($^5D_0 \rightarrow {}^7F_2$). In terms of the Judd-Ofelt theory,[17,18] the electric dipole transition is allowed only when the europium ion occupies a site without an inversion center and is sensitive to local symmetry. The peak around 580 nm corresponds to the $^5D_0 \rightarrow {}^7F_0$ transition, and those near 590 nm derive from the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$). In the emission spectrum of the silica-coated nanoparticles, the peaks at 616 and 623 nm corresponding to the Stark splitting of $^5D_0 \rightarrow {}^7F_2$ transition cannot be resolved due to inhomogeneous broadening. The intensity ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ decreased in silica-coated nanospheres. Generally, the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition can be used as a sensitive parameter to understand the variation in the symmetry of the local environments of Eu^{3+}:[19,20] the higher the ratio, the lower of the symmetry.[21] In addition, after the growth of silica shell material, the emission lines of $^5D_1 \rightarrow {}^7F_J$ ($J = 0$–3) (broad peak from 520 to 560 nm) and $^5D_2 \rightarrow {}^7F_J$ ($J = 0$–2) (peaks at 467, 472, 491 nm) transitions start to appear. These lines indicate the reduced quenching of the $^5D_1$, $^5D_2$ level of the silica-coated europium complex.

4. CONCLUSION

In summary, a facile and effective method for the fabrication of monodisperse silica nanoparticles based on a microemulsion has been proposed. The IR absorption spectra confirm that rare earth (RE) complexs exist in silica spheres. The emission spectra of silica nanoparticles indicate the optical properties of RE complexs have little change. Base on this method, other excellent luminescent RE complex materials can be embedded into conform silica spheres with potential biological application.

References and Notes

1. J. M. Jethmalani and W. T. Ford, *Chem. Mater.* 8, 2138 (**1996**).
2. J. M. Jethmalani, H. B. Sunkara, W. T. Ford, S. L. Willoughby, and B. J. Ackerson, *Langmuir* 13, 2633 (**1997**).
3. J. M. Jethmalani, W. T. Ford, and G. Beaucage, *Langmuir* 13, 3338 (**1997**).
4. W. L. Vos, R. Sprik, A. van Blaaderen, A. Imhof, A. Lagendijk, and G. H. Wegdam, *Phys. Rev. B* 53, 16231 (**1996**).
5. K. Lebbou, P. Perriat, and O. Tillement, *J. Nanosci. Nanotechnol.* 5, 1448 (**2005**).
6. P. A. Tanner, *J. Nanosci. Nanotechnol.* 5, 1455 (**2005**).
7. M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, *Science* 281, 2013 (**1998**).
8. X. Zhao, R. P. Bague, and W. Tan, *Adv. Mater.* 16, 173 (**2004**).
9. D. Zhao, W. Qin, C. Wu, G. Qin, J. Zhang, and S. Lü, *Chem. Phys. Lett.* 388, 400 (**2004**).
10. P. Huhtinen, M. Kivela, O. Kuronen, V. Hagren, H. Takalo, H. Tenhu, T. Lovgren, and H. Harma, *Anal. Chem.* 77, 2643 (**2005**).
11. T. Soukka, H. Harma, J. Paukkunen, and T. Lovgren, *Anal. Chem.* 73, 2254 (**2001**).
12. Z. Ye, M. Tan, G. Wang, and J. Yuan, *Anal. Chem.* 76, 513 (**2004**).
13. M. Tan, Z. Ye, G. Wang, and J. Yuan, *Chem. Mater.* 16, 2494 (**2004**).
14. D. Zhao, W. Qin, J. Zhang, C. Wu, G. Qin, G. De, J. Zhang, and S. Lü, *Chem. Phys. Lett.* 403, 129 (**2005**).
15. M. Ohmori and E. Matijevic, *J. Colloid Interace Sci.* 160, 288 (**1993**).
16. M. Ohmori and E. Matijevic, *J. Colloid Interace Sci.* 150, 594 (**1992**).
17. B. R. Judd, *Phys. Rev.* 127, 750 (**1962**).
18. G. S. Ofelt, *J. Chem. Phys.* 37, 511 (**1962**).
19. C. Wu, W. Qin, G. Qin, D. Zhao, J. Zhang, and S. Huang, *Appl. Phys. Lett.* 82, 520 (**2003**).
20. H. Nabika and S. Deki, *J. Phys. Chem. B* 107, 9161 (**2003**).
21. V. Sudarsan, F. C. J. M. van Veggel, R. A. Herring, and M. Raudsepp, *J. Mater. Chem.* 15, 1332 (**2005**).

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