Effect of Different Surfactants on the Size Control and Optical Properties of Y₂O₃:Eu³⁺ Nanoparticles Prepared by Coprecipitation Method

Abhijit P. Jadhav, Chang Woo Kim, Hyun Gil Cha, Amol Uttam Pawar, Nitin Appa Jadhav, U. Pal,[†] and Young Soo Kang^{*}

Department of Chemistry, Sogang University, Seoul 121-742, Republic of Korea

Received: April 3, 2009; Revised Manuscript Received: May 27, 2009

Nanoparticles of europium-doped yttrium oxide $(Y_2O_3:Eu^{3+})$ were synthesized by coprecipitation method with use of different surfactants like butanol, hexanol, and oleic acid. The as-prepared $Y_2O_3:Eu^{3+}$ samples were annealed at 800 °C and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and UV-visible and photoluminescence (PL) spectroscopy techniques. The nanoparticle shows cubic phase structure. Surfactant helps to inhibit or control the particle growth and avoids agglomeration of nanoparticles effectively by reducing the oxygen bridge bonds between the particles. The most intense red emission peak occurs at 614 nm at an excitation wavelength of $\lambda = 200$ nm. Nanoparticles of $Y_2O_3:Eu^{3+}$ with a particle size of 30 nm synthesized by using oleic acid with NaCl show a 73% rise in PL intensity of the 614 nm peak.

Introduction

Considerable research on upconverting phosphors has been carried out for a long time due to their wide application in various fields. Europium-doped yttrium oxide has attracted much research interest due to its wide applications in display technologies. The phosphor has good luminescent characteristics, acceptable atmospheric stability, reduced degradation under applied voltages, and no hazardous constituents as opposed to sulfide phosphors.¹ In particular, the nanostructured phosphors are of great interest as they offer brighter cathodoluminescence and much improved screen packing.² Inorganic nanoparticles manifest unique size and shape dependent properties, which to some extent depend on their crystallinity, defect contents, and preparation techniques. Y₂O₃:Eu³⁺ nanostructures of different morphologies have been synthesized by using different methods such as gas phase condensation technique,³ sol-gel route,^{4,5} homogeneous precipitation,⁶ spray pyrolysis,⁷ and hydrothermal method.8

Phosphor particles should have a spherical shape and high luminescence efficiency for their successful applications as they are capable of minimizing light scattering on their surfaces improving the efficiency of light emission and the brightness of a phosphor screen.9,10 However, the shape and size of luminescent particles depend on their synthesis method. Phosphor particles synthesized by different methods show variation in their size, shape, and optical properties. For example, the phosphor particles prepared by solid state reaction have irregular shape and surface damage, which acts as a nonradioactive transition center, decreasing their luminescence efficiency.⁶ On the other hand, the synthesis of Y₂O₃:Eu³⁺ nanoparticles by coprecipitation methods is simpler and does not require heating. Coprecipitation synthesis involves dissolution of compound salt precursor in aqueous media and subsequent precipitation from the solution by pH adjustment. Apart from its simplicity, atomic mixing of the constituents by chemical coprecipitation yields a final product of near-perfect stoichiometry without hightemperature treatment. The chemical coprecipitation begins by dissolving the starting oxides in an acid solution or salts in aqueous medium. The solution is then mixed with another solution of dissolved precipitating agent to precipitate the mixed oxalate or hydroxide out of solution. The final crystalline oxide is obtained by firing the precipitates at a higher temperature.¹¹ The surfactant used in the synthesis helps to control the grain growth and agglomeration of particles efficiently. Surfactant also reduces the oxygen bridge bonds between particles and avoids agglomeration efficiently.¹² The sintering process plays an important role in controlling the particle size through agglomeration. Hydrogen bonds between chemically combined OH⁻ resulting in the formation of oxygen bridge bonds have been cited as the main reason for such hard agglomeration.^{13,14}

He et al. have carried out the synthesis of Y_2O_3 :Eu³⁺ phosphors using butanol as a surfactant. Addition of butanol as a surfactant inhibits the grain growth and the efficiency of particle agglomeration by reducing the oxygen bridge bonds. On the other hand, the pH of the medium also plays an important role in controlling the photoluminescence (PL) intensity and particle size of the phosphor.¹²

In this work we synthesized Y_2O_3 :Eu³⁺ phosphor nanoparticles using different kinds of surfactant such as butanol, hexanol, oleic acid, and oleic acid–NaCl mixture. Y_2O_3 :Eu³⁺ phosphors were synthesized by using oleic acid show narrow particle size distribution in the range of 100–120 nm. The nanoparticles were studied for their structural and emission (PL) behaviors. The effect of NaCl addition on the particle size, size distribution, and emission behavior of the nanophosphors has been studied.

Experimental Section

Materials. Yttrium oxide $((Y_2O_3) 99.99\%$ Sigma Aldrich), europium oxide $((Eu_2O_3), 99.9\%)$, Sigma Aldrich), sodium carbonate $((Na_2CO_3), Junsei$ Chemicals Co. Ltd.), sodium chloride ((NaCl), Duksan Pure Chemical Co. Ltd.), butanol

^{*} To whom correspondence should be addressed. Phone: +82 2 705 8882. Fax: +82 2 701 0967. E-mail: yskang@sogang.ac.kr.

 $^{^{\}dagger}$ On leave from Instituto de Física, Universidad Autónoma de Puebla, Mexico.

Optical Properties of Y₂O₃:Eu³⁺ Nanoparticles

(($C_4H_{10}O$), Junsei Chemicals Co. Ltd.), hexanol (($C_6H_{13}OH$), Junsei Chemicals Co. Ltd.), oleic acid (($C_{18}H_{34}O_2$), Junsei Chemicals Co. Ltd.), and hydrochloric acid ((HCl), Jin Chemicals Pharmaceuticals Co. Ltd.) were used as received without further purification.

Synthesis. For the synthesis of Y_2O_3 :Eu³⁺ phosphor by the coprecipitation method, oxides of yttrium and europium, i.e., Y_2O_3 and Eu₂O₃, were converted into their chloride salts (YCl₃•6H₂O and EuCl₃•6H₂O) by adding hydrochloric acid. The reactions that occurred in the process are given below:

$$Y_2O_3 + 6HCl \rightarrow 2YCl_3 + 3H_2O \tag{1}$$

$$Eu_2O_3 + 6HCl \rightarrow 2EuCl_3 + 3H_2O \qquad (2)$$

The chloride precursors were prepared by addition of 65.0 mL of HCl (37%, 1 M) with 10.24 mmol of Y_2O_3 and 3.87 mmol of Eu_2O_3 , respectively. Clear solutions were formed after the addition of HCl. The mixture solutions were then heated at 80 °C and solid YCl₃•6H₂O and EuCl₃•6H₂O were collected from the bottom of the container.

In a typical coprecipitation synthesis, 95.0 mmol of $YCl_3 \cdot 6H_2O$ (0.725 g) and 5.0 mmol of $EuCl_3 \cdot 6H_2O$ (0.05 g) were mixed in 50.0 mL of DI water and 1.0 mL of surfactant under vigorous magnetic stirring for 2 h. While using NaCl with oleic acid as surfactant, 0.436 g (7.46 mmol) of NaCl was added to the first solution during the synthesis. The precipitation of the complex oxalate from the solution was carried out by dropwise addition of an aqueous Na₂CO₃ solution (0.3 × 10⁻³ M) maintaining the final pH at 7.0. A white precipitate was formed on addition of the Na₂CO₃ solution (eq 3). The obtained product was washed repeatedly with DI water and separated by filtration.

$$YCl_{3} + EuCl_{3} + Na_{2}CO_{3} \xrightarrow{\text{surfactant}} Y_{2}C_{2}O_{4}:Eu_{2}C_{2}O_{4} + NaCl + CO_{2} + O_{2} \quad (3)$$

The as-prepared complex was dried at 80 °C for 6 h in air ambient and then annealed in air at 800 °C for 1 h with use of a muffle furnace. On annealing, the complex structure is converted into oxide (eq 4).

$$Y_2C_2O_4:Eu_2C_2O_4 \xrightarrow{800^{\circ}C} Y_2O_3:Eu^{3+}$$
(4)

Characterizations. The size and shape of the synthesized nanoparticles were examined with JEOL, JEM-2010, and JEOL JEM 2100F transmission electron microscopes operating at 200 kV. For TEM observations, a small amount of the powder sample was dispersed into cyclohexane and a drop was placed over a carbon coated microscopic copper grid (300 mesh size). The TEM grid was then dried under a UV lamp. The surface morphology of the as-synthesized and annealed samples was studied with use of a field emission scanning electron microscope (FE-SEM, JEOL LTD JSM 890). The powder X-ray diffraction patterns of the as-prepared and annealed samples were recorded with use of the Cu K α radiation ($\lambda = 1.54056$ Å) of a Rigaku X-ray diffractometer at a scanning rate of 0.02° per second in the 2θ range of $10^\circ \le 2 \theta \le 80^\circ$. The X-ray diffractometer was operated at 40 kV and 150 mA. The room temperature photoluminescence (PL) of the powder samples was



Figure 1. XRD patterns of Y_2O_3 :Eu³⁺ nanoparticles synthesized with (a) butanol, (b) hexanol, (c) oleic acid, and (d) oleic acid with NaCl as surfactants. The peaks positions are compared with the standard (JCPDS card 25-1011) at the bottom.

measured with a Hitachi F-7000 fluorescence spectrophotometer, using the 200 nm excitation of a Xenon lamp.

Results and Discussion

The XRD patterns of $Y_2O_{3(0.095)}$:Eu³⁺(0.005) nanoparticles synthesized by using different surfactants and annealed at 800 °C are shown in Figure 1. The diffraction peaks appeared at 2θ = 20.6°, 29.2°, 31.5°, 33.8°, 48.5°, 57.6°, and 78.8° correspond to the (211), (222), (321), (400), (440), (622), and (653) planes of the body centered cubic structure of Y_2O_3 :Eu³⁺. The high intensity of the diffraction peaks indicates good crystallinity of the nanoparticles.

Figure 2 shows the EDS spectra of Y_2O_3 :Eu³⁺ nanoparticles synthesized with different surfactants. The existence of Eu in the samples is clear in their corresponding EDS spectra. There appeared no other emissions apart from Y, Eu, O, Cu, and C in the EDS spectra of the samples. The elemental compositions of the samples in atomic percent are given in Table 1. The Y and Eu atomic ratio in the samples was about 95:5, which is close their nominal compositions ($Y_{2(0.095)}$ Eu (0.005) O₃). Given the fact that the existence of C and Cu is from the copper grid used in the characterization, it is easy to see the effective incorporation of the Eu³⁺ into the matrix.

Figure 3 shows the XPS survey spectra of Y_2O_3 :Eu³⁺ samples synthesized with different surfactants. The XPS spectra revealed the emission peaks correspond to Y, O, C, and Eu in the synthesized samples. The calibration of the energy scale was done by using the C1s peak at 284.6 eV as a reference. The calibration of the energy scale is important as sample charging took place for the materials under investigation.²⁵ XPS is a wellknown surface-sensitive characterization method. The surface composition obtained is actually a composition of the Y₂O₃: Eu³⁺ particle's surface that was synthesized by using different surfactants, which is shown in Table 2. According to the data represented in Table 2 we observed that the Y:Eu³⁺ ratio increases from the sample prepared by using butanol to oleic acid with NaCl. The typical O1s core level XPS spectrum for the Y₂O₃:Eu³⁺ sample synthesized with oleic acid and NaCl is shown in Figure 4. The spectrum consists of a main peak at about 533.23 eV and a subpeak at about 531.07 eV. While the main peak is attributed to O^{2-} bonded to Y^{3+} , the subpeak represents the bonding between O^{2-} and Eu^{3+} .¹⁵

Figure 5 shows the TEM images of Y_2O_3 :Eu³⁺ nanoparticles synthesized with different surfactants and annealed at 800 °C.



Figure 2. EDS spectra of the annealed Y_2O_3 : Eu³⁺ nanoparticles prepared with (a) butanol, (b) hexanol, (c) oleic acid, and (d) oleic acid with NaCl as surfactants.

 TABLE 1: EDS Estimation of Elemental Composition for

 the Nanophosphors Prepared with Different Surfactants

surfactant	Y (atom %)	Eu (atom %)	Y:Eu (atomic ratio)
butanol	47.05 ± 0.337	3.06 ± 0.165	15.38
hexanol	40.88 ± 0.212	1.86 ± 0.096	21.98
oleic acid	45.45 ± 0.303	2.66 ± 0.141	17.09
oleic acid and NaCl	41.94 ± 0.282	1.93 ± 0.127	21.73

Formation of nanoparticles of homogeneous size in all the samples is clear from their corresponding images. Formation of $Y_2O_3:Eu^{3+}$ nanoparticles of about 60 nm average size has been reported by He using butanol as a surfactant.¹² In our case, use of butanol produced $Y_2O_3:Eu^{3+}$ nanoparticles of about 30 nm average size (Figure 5a). $Y_2O_3:Eu^{3+}$ synthesized with hexanol and oleic acid produced nanoparticles in the 72 and 125 nm size range of diameters (Figure 5b,c), respectively. However, the shape, size, and size distribution of the particles depended on the nature of the surfactant used. It has been



Figure 3. XPS survey spectra of Y_2O_3 :Eu³⁺ nanoparticles synthesized with (a) butanol, (b) hexanol, (c) oleic acid, and (d) oleic acid with NaCl. All the samples were annealed at 800 °C in air for 1 h.

TABLE 2: Surface Composition of the Y_2O_3 :Eu ³⁺	
Nanoparticles Synthesized with Different Surfactan	ts
Estimated through XPS Analysis	

surfactant	Eu ³⁺ (atom %)	O (atom %)	Y (atom %)	Y:Eu ³⁺ atomic ratio
butanol	0.80	65.53	33.57	41.96
hexanol	0.49	73.70	25.82	52.69
oleic acid	0.23	84.45	15.52	67.47
oleic acid with NaCl	0.49	64.41	35.10	71.63

observed that the use of a water insoluble surfactant like oleic acid produces a narrow particle size distribution. Oleic acid reduces the oxygen bridge bonds between the particles and avoids hard agglomeration efficiently.¹² An oleic acid and NaCl mixture produced the most homogeneous nanoparticles of about 30 nm average size (Figure 5d). The observed particle size ranges for the Y₂O₃:Eu³⁺ synthesized with different surfactants are given in Table 3.

The room temperature PL spectra of the nanostructures synthesized with different surfactants are shown in Figure 6.



Figure 4. O1s spectrum of the annealed Y_2O_3 :Eu³⁺ nanoparticles synthesized with oleic acid and NaCl.



Figure 5. Typical TEM images of the Y_2O_3 :Eu³⁺ nanoparticles prepared with (a) butanol, (b) hexanol, (c) oleic acid, and (d) oleic acid with NaCl as surfactant. All the samples were annealed at 800 °C in air for 1 h. Size distribution histograms of the samples are presented as insets of the corresponding TEM images.

TABLE 3: Variation of Particle Size and PL Intensity of the Y_2O_3 :Eu³⁺ Nanoparticles Synthesized with Different Surfactants

surfactant	av particle size (nm); standard dev (nm)	intensity of the 614 nm emission peak (au)
butanol	30.5; 8.1	2449.78
hexanol	72.7; 24.9	956.84
oleic acid	125.3; 26.4	7721.60
oleic acid and NaCl	30.1; 5.0	23396.00

There appeared a strong emission peak at about 614 nm and two weak emissions at about 630 and 594 nm. The strong emission band appearing at about 614 nm is commonly assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in Eu³⁺ ions,¹⁶ whereas the shoulder peaks appearing at about 594 and 630 nm correspond to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transitions, respectively.¹⁷

The host Y_2O_3 crystal has a cubic unit cell structure with space group *Ia*3, where ${}^{3}/_4 Y^{3+}$ ion occupies the low symmetric C_2 site and ${}^{1}/_4 Y^{3+}$ occupies the high symmetric S_6 site. If the activator Eu^{3+} ions in the host dominantly occupy the site with low symmetry, the selection rule will be partially broken. As a result, the emission at 614 nm will be strengthened greatly, and the 594 nm emission from the ${}^5D_0 \rightarrow {}^7F_1$ transition will be weakened remarkably.^{18–22} The PL spectrum of our $Y_2O_3:Eu^{3+}$ nanoparticles synthesized with oleic acid and NaCl shows maximum luminescence intensity, which is contrary to the observation of Yan, who has reported a slight decrease of emission intensity on the addition of NaCl in the reaction solution.²³ In our case, the addition of NaCl with oleic acid showed an ca. 73% increase in PL intensity of $Y_2O_3:Eu^{3+}$ in comparison with the emission intensity of the nanoparticles



Figure 6. Room temperature PL spectra of the Y_2O_3 :Eu³⁺ nanoparticles prepared with (a) butanol, (b) hexanol, (c) oleic acid, and (d) oleic acid with NaCl as surfactant. For excitation 200 nm emission of a xenon lamp was used.

synthesized with oleic acid only. In earlier reports a 45% rise in luminescence intensity was reported by Yan et al.²³ After the addition of NaCl the PL intensities of the most intense peak (614 nm) of Y_2O_3 :Eu³⁺ nanoparticles synthesized with different surfactants are presented in Table 3.

Addition of NaCl plays an important role in controlling the particle size of the Y_2O_3 :Eu³⁺ nanophosphor. As has been observed from the TEM micrographs, addition of NaCl along with oleic acid produces Y_2O_3 :Eu³⁺ nanoparticles with narrow particle size distribution. The dissolved salt forms an adsorbed layer over the surface of the precipitating nanoparticles. This

adsorbed layer restricts the growth of nanoparticles avoiding their agglomeration.^{23,24} It has been reported that the Na⁺ and Cl⁻ ions form the double electric layer at the liquid membranes over the nanoparticles preventing their further growth.²⁵ As NaCl has good solubility in water, it can be removed easily by washing the samples in water rendering no possibility of contamination. As has been mentioned earlier, addition of NaCl also increased the PL intensity of our Y₂O₃:Eu³⁺ nanophosphors. We believe that the addition of NaCl in the reaction mixture helps to promote the diffusion of Y3+ and Eu3+ during the growth of Y₂O₃:Eu³⁺ nanoparticles, which in turn helps to maintain the proportion of Eu³⁺ in the samples, promoting better crystallization and reducing surface defects. As can be seen from Figure 6, addition of NaCl in the reaction mixture enhanced the PL intensity of the nanoparticles about two times in comparison with that of the nanoparticles prepared with oleic acid only.

As has been mentioned earlier, the synthesis of $Y_2O_3:Eu^{3+}$ nanoparticles has been carried out with butanol, hexanol, and oleic acid as surfactants. Water is a polar solvent that attracts the –OH group. Butanol and hexanol molecules have a nonpolar carbon chain and a polar –OH terminal group. Hence, their solubility in water is limited. On the other hand, their larger alkyl groups will interfere with the hydrogen bonds of water molecules strongly, causing an increase in the van der Waals force.²⁶ The solubility of butanol in water is 1.006 mol kg⁻¹ (9.1 mL/100 mL of H₂O at 25 °C), and for hexanol it is 0.061 mol kg⁻¹ (590 mg/100 mL of H₂O at 25 °C).²⁷ During the coprecipitation process, the surfactant butanol or hexanol is added to the aqueous solution containing yttrium and europium salts.

Oleic acid is hydrophobic in nature. At low concentration, randomly moving oleic acid molecules in water form a layer over the nanoparticles through a chemical or physical adsorption process, facing the hydrophobic groups toward the aqueous phase. This adsorption leads to the increase of hydrophobicity of the particle surface.²⁵ The addition of Na₂CO₃ as a precipitating agent results in the formation of the complex structure Y₂C₂O₄:Eu₂C₂O₄. Washing precipitated nanoparticles will remove the soluble byproducts. The organic part present in the precipitated product will be removed during the annealing process and Y₂O₃:Eu³⁺ phosphor will be formed after annealing at 800 °C. Addition of NaCl with oleic acid results in the formation of sodium oleate, which is more soluble (100 mg/ mL at 25 °C)²⁸ in water than only oleic acid (which is insoluble in water)²⁹ and helps to obtain homogeneous phosphor particles during precipitation.

Conclusion

In summary, $Y_2O_3:Eu^{3+}$ nanophosphors were synthesized with various surfactants such as butanol, hexanol, oleic acid, and oleic acid–NaCl mixture. The highly crystalline, monodispersed nanoparticles have high PL emission at room temperature. While the use of oleic acid alone produces $Y_2O_3:Eu^{3+}$ nanoparticles of largest size, $Y_2O_3:Eu^{3+}$ nanoparticles synthesized with oleic acid and NaCl together are smallest in size, with the best homogeneous size distribution and maximum emission efficiency. Addition of NaCl as co-additive along with oleic acid has shown an improvement in the size homogeneity and reduces surface defects in Y_2O_3 :Eu³⁺ nanophosphors. We have demonstrated that the red emitting Y_2O_3 :Eu³⁺ nanophosphors of particle size in the 30 nm range with high PL emission can be prepared through the coprecipitation method with oleic acid and NaCl mixture as surfactant.

Acknowledgment. This work was financially supported by Energy Technology Research and Development 2008 and the Brain Korea 21.

References and Notes

(1) Bhargava, R. N. J. Lumin. 1996, 70, 85.

(2) Martinez-Rubio, M. I.; Ireland, T. G.; Fern, G. R.; Silver, J.; Snowden, M. J. *Langmuir* 2001, *17*, 7145.

(3) Williams, D. K.; Yuan, H. B.; Tissue, B. M. J. Lumin. 1999, 83, 297.

(4) Guo, H.; Zhang, W.; Lou, L.; Brioude, A.; Mugnier, J. *Thin Solid Films* **2004**, 458, 274.

(5) Zhang, J. L.; Hong, G. Y. J. Solid State Chem. 2004, 177, 1292.
(6) Wakefield, G.; Holland, E.; Dobson, P. J.; Hutchison, J. L. Adv. Mater 2001, 13, 1557.

(7) Dosev, D.; Guo, B.; Kennedy, I. M. J. Aerosol Sci. **2006**, *37*, 402.

(8) Wang, X.; Li, Y. D. Angew. Chem., Int. Ed. **2002**, 41, 4790.

(9) Yoo, J. S.; Lee, J. D. J. Appl. Phys. **1997**, 81, 2810.

(10) Vila, L. D.; Stucchi, E. B.; Davolos, M. R. Eur. J. Mater. Chem. 1997, 7, 2113.

(11) Wang, Z. L.; Liu, Y.; Zhang, Z. Handbook of Nanophase and Nanostructured Materials; Tsinghua University Press: New York, 2003; Vol. 1.

(12) He, C.; Guan, Y.; Yao, L.; Cai, W.; Yao, Z. Mater. Res. Bull. 2003, 38, 973.

(13) Jones, S. L.; Norman, C. J. J. Am. Ceram. Soc. 1998, 71, c-1909.
(14) Shi, J. L.; Gao, J. H.; Lin, Z. X.; Yen, T. S. J. Mater. Sci. 1993, 28, 342.

(15) Bae, J. S.; Yoon, J. H.; Park, S. K.; Kim, J. P.; Jeong, E. D.; Won, M. S.; Shim, K. S.; Yang, H. K.; Yi, S. S.; Jeong, J. H. *Surf. Rev. Lett.* **2007**, *4*, 535.

(16) Li, Q.; Gao, L.; Yan, D. S. Wuji Cailiao Xuebao 1997, 12 (2), 237.

(17) Jia, P. Y.; Lin, J.; Han, X. M.; Yu, M. *Thin Solid Films* **2005**, *483*, 122.

(18) Anh, V. N.; Yi, G. C.; Streak, W. J. Lumin. 2007, 776, 122.

(19) Shionoya, S.; Yen, W. M.; Takashi, H. *Phosphor Handbook*; CRC Press: Boca Raton, FL, 1999; p 112.

(20) Butler, K. H. Fluorescent Lamp Phosphors Technology and Theory; The Pennsylvania State University Press: University Park, PA, 1980; p 15.

(21) Yu, Z.; Huang, X.; Zhuang, W.; Cui, X.; He, H.; Li, H. J. Rare Earths 2004, 22 (6), 829.

(22) Shin, S. H.; Kang, J. H.; Jeon, D. Y.; Zang, D. S. J. Lumin. 2005, 114 (34), 275.

(23) Yan, H.; Yunsheng, H.; Xiaoming, T.; Zhen, L.; Hongqi, Y.; Weidong, Z. J. Rare Earths 2007, 25, 697.

(24) Yan, H.; Hongqi, Y.; Weidong, Z.; Yunsheng, H.; Chunlei, Z.; Cui, L.; Songxia, G. *Trans. Nonferrous Met. Soc. China* **2007**, *17*, 644.

(25) Jun, R.; Shouci, L.; Jian, S.; Boxing, H. Chin. Sci. Bull. 45 2000, 15, 1376–1380.

(26) Sterner, O. Chemistry, Health and Environment; Wiley-VCH: New York, 1999; p 41.

(27) Florence, A. T. Attwood, D. *Physicochemical Principles of Pharmacy*, 4th ed.; Pharmaceutical Press: London, UK, 2006; p 142.

(28) The Merck Index: An Encyclopedia of Chemicals, Drugs and Biologicals, 12th ed.; Budavari, S., O'Neil, M. J., Eds.; Merck & Co., Inc.: Rahway, NJ, 1996.

(29) The Merck Index: An Encyclopedia of Chemicals, Drugs and Biologicals, 11th ed.; O'Neil, M. J., Ed.; Merck & Co., Inc.: Rahway, NJ, 1998; pp 1079-1080.

JP903067J