

Synthesis of $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell materials and hollow spheres

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Abstract

The $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell materials and hollow spheres were first synthesized by a template-mediated method. X-ray diffraction patterns indicated that the broadened diffraction peaks result from nanocrystals of $\text{Y}_2\text{O}_3:\text{Eu}$ shells and hollow spheres. X-ray photoelectron spectra showed that the $\text{Y}_2\text{O}_3:\text{Eu}$ shells are linked with silica cores by Si–O–Y chemical bond. SEM and TEM observations showed that the size of $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell structure is in the range of 140–180 nm, and the thickness of $\text{Y}_2\text{O}_3:\text{Eu}$ hollow spherical shell is about 20–40 nm. The photoluminescence spectra of $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell materials and $\text{Y}_2\text{O}_3:\text{Eu}$ hollow spheres have better red luminescent properties, and the broadened emission bands came from the size effects of nanocrystals composed of $\text{Y}_2\text{O}_3:\text{Eu}$ shell.

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Keywords: $\text{Y}_2\text{O}_3:\text{Eu}$; Core-shell; Hollow spheres; Luminescence properties

1. Introduction

Nanometer- and micrometer-sized core-shell structure particles and hollow spheres with special physical and chemical properties have attracted great attention due to their potential applications in photonic crystals, catalyst, diagnostics, pharmacology, etc. [1–3]. In particular, inorganic hollow nanospheres with well-defined architectures are of great increasing interest due to their low density, high surface area, stability, and surface permeability, they may find a wide range of applications as catalysis, shape-selective adsorbents, chemical sensors and capsules for controlled release of therapeutic agents [4–8]. A number of methods have been employed to synthesize the core-shell materials and hollow spheres, for example, the interface assembly strategies [9,10], layer-by-layer self-assembly processes [11], hydrothermal and solvothermal precipitation method [12,13]. The most common route for preparing hollow spheres is sacrificial template method; the process is to coat the

desired materials on the template cores to form core-shell spheres and then removing the template by either calcinating in air or selective etching with a solvent. The common template materials are polymer colloids and inorganic colloids such as polystyrene colloids and silica, Ag or Au nanoparticles.

For example, Yang et al. [14] used sulfonated polystyrene core-shell gel particles as templates to prepare hollow titania spheres. Xu et al. [15] used silica particles as template to fabricate polymer hollow spheres by dispersion polymerization around monodispersed silica particles, and then removed the silica cores by HF etching. Recently, we have synthesized $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}$ core-shell luminescent materials by coating $\text{Gd}_2\text{O}_3:\text{Eu}$ on silica nanoparticles with homogeneous precipitation method [16]. It is well known that $\text{Y}_2\text{O}_3:\text{Eu}$ is a kind of widely used red phosphor and display material, it has also been used as luminescent probe for high sensitivity of Eu^{3+} ions to their surroundings. $\text{Y}_2\text{O}_3:\text{Eu}$ with different morphology such as spherical nanocrystal and nanotubes has been prepared [17–20], but the core-shell structure $\text{Y}_2\text{O}_3:\text{Eu}$ and hollow spheres have not been prepared. The core-shell structure and

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hollow spheres of $\text{Y}_2\text{O}_3:\text{Eu}$ red phosphors will achieve a reduction in the amount of expensive rare earth, additionally, due to the low density of hollow spherical materials, when coating screen in display applications, the phosphors can be dispersed well, enhance the uniformity and give high packing densities of the coating. In this paper, we prepared $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell structure materials by using silica spheres as template, and dissolved silica cores with sodium hydroxide to obtain $\text{Y}_2\text{O}_3:\text{Eu}$ hollow spheres. The core-shell structure and hollow spherical $\text{Y}_2\text{O}_3:\text{Eu}$ still has retained red luminescent properties.

2. Experimental section

The $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell materials and hollow spheres were synthesized by silica spheres as template. The template silica was prepared according to Ref. [16]. The homogeneous precipitation method was used to coat europium-doped yttria on silica, and then dissolved

the silica template to obtain hollow spheres. The detailed procedure was as follows: First, yttrium oxide (99.99%) and europium oxide (99.99%) were dissolved in a minimum amount of diluted nitric acid (1:1), evaporated to dryness, cooled to room temperature, then dissolved in distilled water to form yttrium nitrate and europium nitrate solutions. Secondly, a certain amount of prepared SiO_2 cores were ultrasonically dispersed in the stock solutions containing $0.02 \text{ mol L}^{-1} \text{ Y}(\text{NO}_3)_3$, $0.001 \text{ mol L}^{-1} \text{ Eu}(\text{NO}_3)_3$ ($\text{Eu}/\text{Y} = 5 \text{ at}\%$) and $2 \text{ mol L}^{-1} (\text{NH}_2)_2\text{CO}$. The dispersion was then aged at $85\text{--}90^\circ\text{C}$ in tightly capped beaker under continuous stirring for 5 h. Then the resulting product was filtered and washed with distilled water for three times. The samples were heated at 800°C in air for 2 h after being dried at 80°C for 2 h and then the core-shell materials were obtained. At last, the core-shell materials were dispersed in $1 \text{ mol L}^{-1} \text{ NaOH}$ solutions for 12 h, and washed with distilled water until the pH value is equal to 7, dried for 12 h and obtained the hollow spheres.

The sample structure was detected by a RIGAKU D/max-IIB X-ray diffractometer. Particles' surface element binding energy and chemical composition were characterized by a VGESCALAB MK II X-ray photoelectron spectrometer. The morphologies of samples were observed using a PHILIPS XL30 ESEM FEG scanning electron microscopy (SEM) and a JEOL JEM-2010 transmission electron microscopy (TEM). The excitation and emission spectra of the samples were measured by a HITACHI F-4500 fluorescence spectrophotometer using an Xe lamp as the excitation source.

3. Results and discussion

3.1. XRD patterns

The X-ray diffraction (XRD) patterns of silica cores, the $\text{Y}_2\text{O}_3:\text{Eu}$ -coated silica calcinated at 800°C and the calcinated samples etched by NaOH are shown in Figs. 1a–c. The silica cores are amorphous as evident

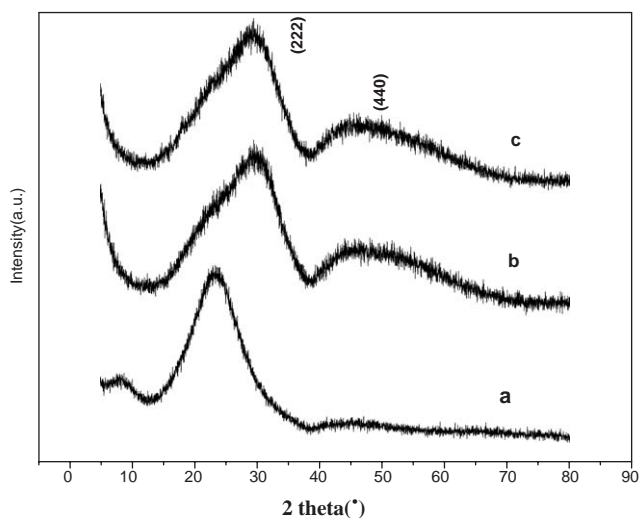


Fig. 1. XRD patterns of SiO_2 cores (a), $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ calcinated at 800°C (b), the calcinated sample etched by NaOH (c).

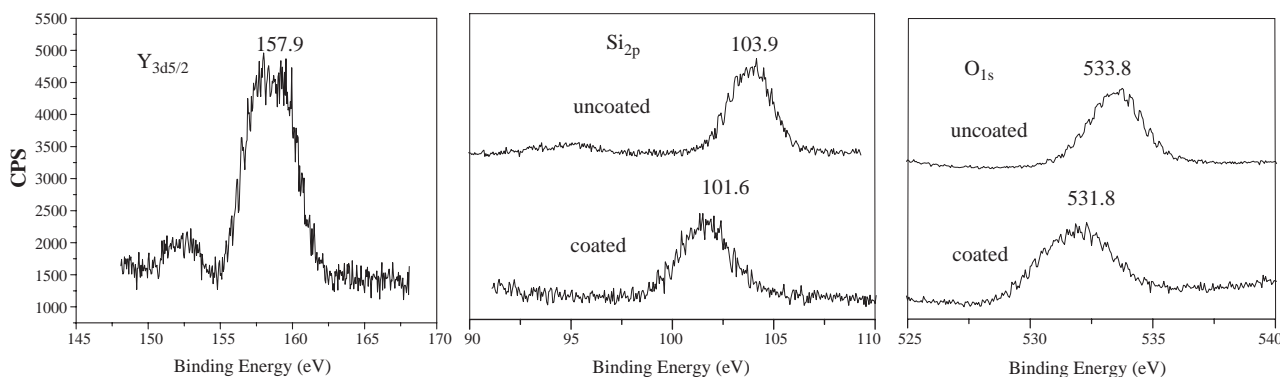


Fig. 2. XPS spectra of $\text{Y}_{3d5/2}$, Si_{2p} and O_{1s} of bare silica cores and $\text{Y}_2\text{O}_3:\text{Eu}$ -coated silica core-shell structure materials.

from the presence of a broader hump in Fig. 1(a). The curve (b) is the pattern of the $\text{Y}_2\text{O}_3\text{:Eu}$ -coated silica, there are two broadened diffraction peaks which coincide with the peaks of cubic yttria assigned as (222) and (440) reflection lines, respectively, which indicates that crystalline Y_2O_3 has been formed on the surface of silica, the broadened diffraction peaks are probably due to the nanometer grain sizes and the effects of the amorphous silica cores. In curve (c), after the samples etched by sodium hydroxide, the peak of silica disappears and the peaks of cubic yttria are not changed, this indicates that the hollow shells are crystalline Y_2O_3 nanoparticles.

3.2. XPS spectra

In order to study the combination of silica cores and $\text{Y}_2\text{O}_3\text{:Eu}$ shells of core-shell structure materials, X-ray photoelectron spectra (XPS) of samples are measured. The XPS spectra of $\text{Y}_{3d5/2}$, Si_{2p} and O_{1s} of bare silica cores and $\text{Y}_2\text{O}_3\text{:Eu}$ -coated silica core-shell structure materials are shown in Fig. 2. From Fig. 2a, the peak of $\text{Y}_{3d5/2}$ (157.9 eV) can be seen on $\text{Y}_2\text{O}_3\text{:Eu}$ -coated silica core-shell structure materials, which comes from the $\text{Y}_2\text{O}_3\text{:Eu}$ coatings. From Fig. 2b and c, the binding energy of Si_{2p} and O_{1s} of $\text{Y}_2\text{O}_3\text{:Eu}$ -coated silica core-shell particles is lowered to that of the bare silica particles by 2.3 and 2.0 eV, respectively. It is inferred that $\text{Y}_2\text{O}_3\text{:Eu}$ is linked to the surface of silica by a Si–O–Y chemical bond. Because the electronegativity of Y is lower than that of Si, which strengthens the electronic density on the surface of Si, then the shielding effect of the surface is strengthened, and the binding energy of Si_{2p} is lowered. For O_{1s} , the forming Si–O–Y bond on the surface of the particles makes the electronic density of O combined with Si increase, so the binding energy of O_{1s} for core-shell particle has a chemical shift of -2.0 eV.

3.3. Electron microscopic studies

The image of silica cores is shown in Fig. 3(a). From the photograph, we can see that the core particles of silica are all in spheres and the size of particles is uniform in the range of 120–140 nm. After coating with the europium-doped yttria, the microscopy is shown in Fig. 3(b), noted that it is still spherical, but the surface of core-shell structure particles is rougher than that of bare silica cores, and the particle size is larger than that of the bare silica cores and increased to 140–180 nm, which indicates that the thickness of coating is about 20–40 nm. From Fig. 3(c), the SEM microscopy of calcinated samples etched by sodium hydroxide, the particles are still in spheres, and they are partly agglomerated as a result of the heat treatment. In addition, there are some void in the particles directed by

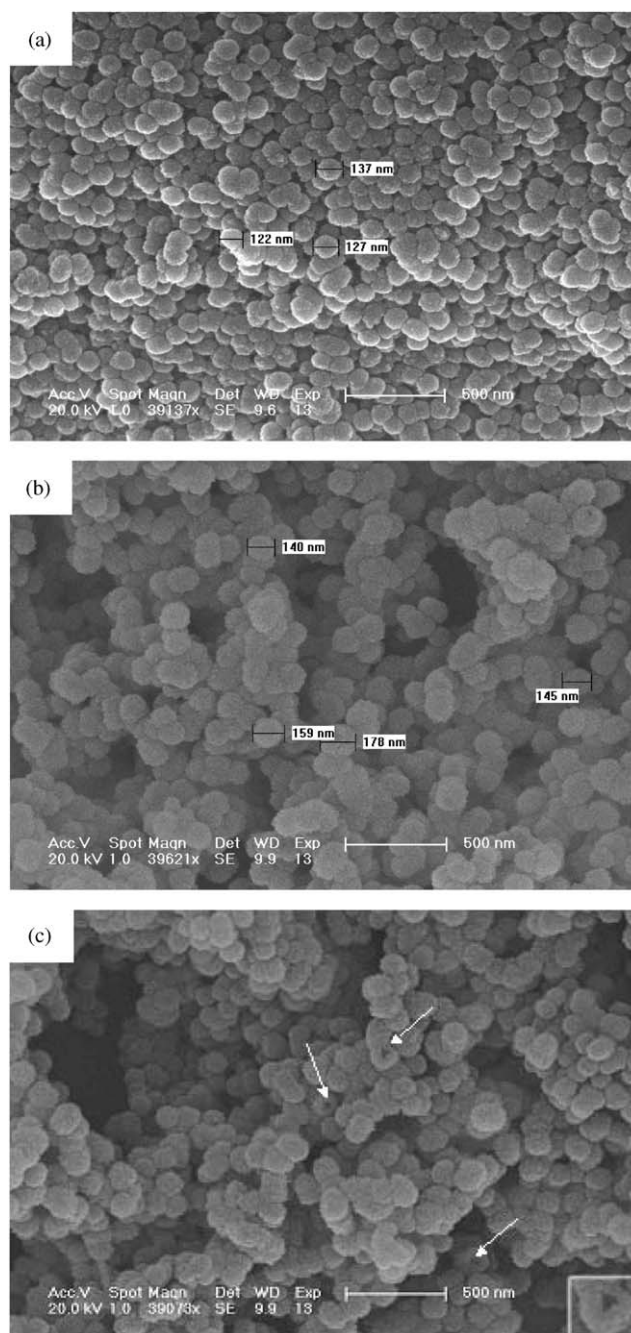


Fig. 3. SEM micrographs of the silica cores (a), $\text{Y}_2\text{O}_3\text{:Eu}$ -coated silica (b) and the calcinated samples etched by sodium hydroxide (c).

arrows and the inset magnified image, which conforms that the hollow spheres are obtained by etching of sodium hydroxide.

Fig. 4 shows the TEM images of samples etched by sodium hydroxide. Note that the samples are partly in core-shell structures and partly in hollow spheres, the thickness of shells is about 20 nm, which is conformed by the magnified image of Fig. 4(b). The difference in contrast between the particles of TEM photographs is

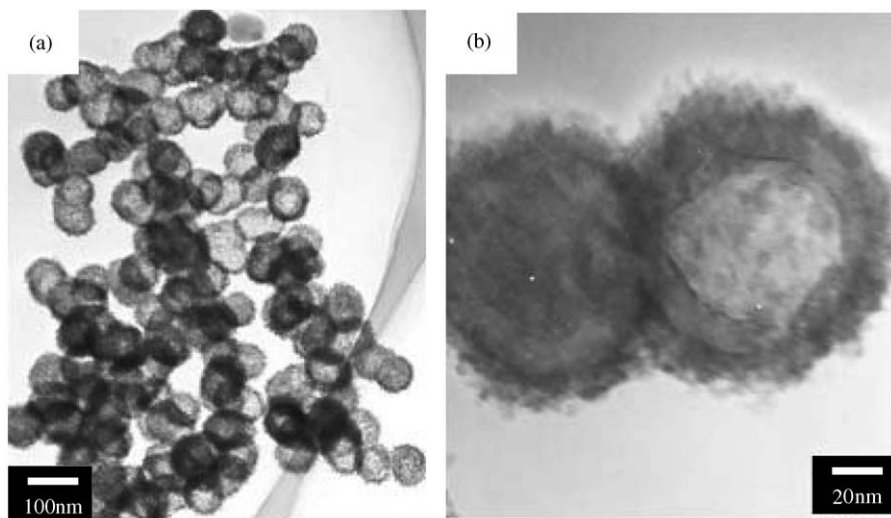
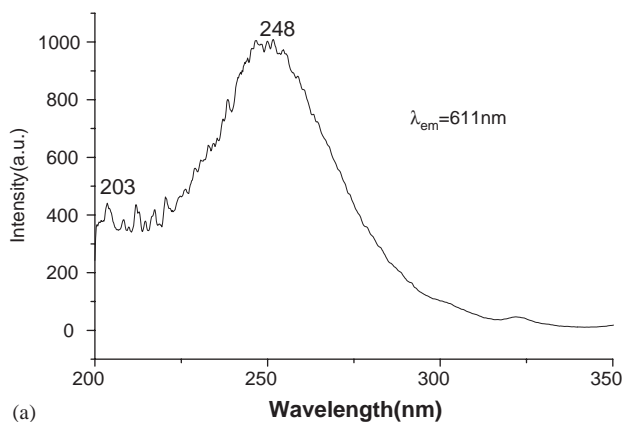
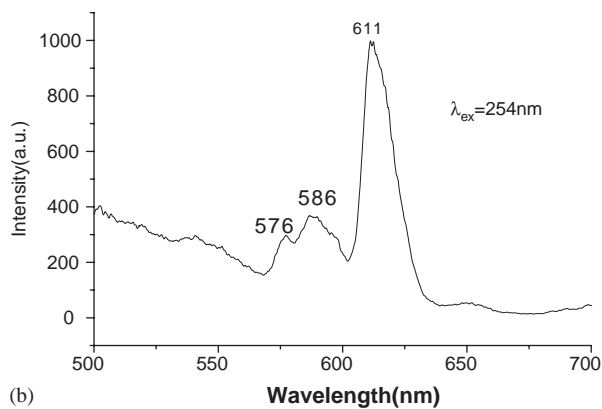


Fig. 4. TEM micrographs of calcinated sample etched by sodium hydroxide: (a) the entire image; (b) the magnified image.

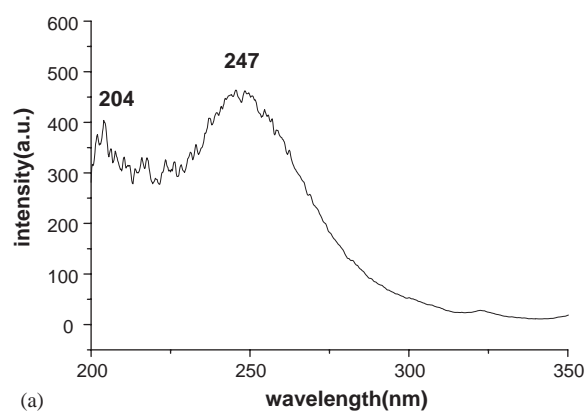


(a)

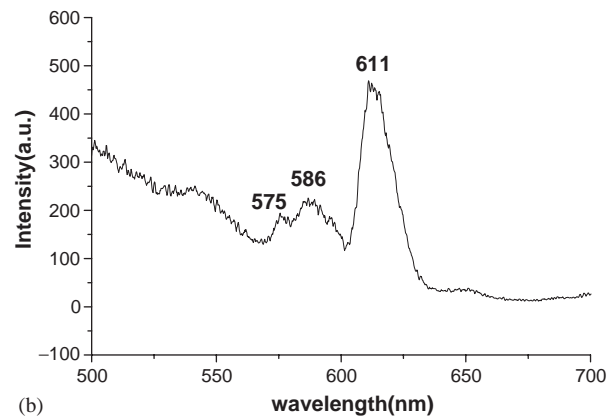


(b)

Fig. 5. The excitation spectrum (a) and emission spectrum (b) of $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell structure materials.



(a)



(b)

Fig. 6. The excitation spectrum (a) and emission spectrum (b) of $\text{Y}_2\text{O}_3:\text{Eu}$ hollow spheres.

due to incomplete etching of silica cores by sodium hydroxide for some core-shell particles. In addition, it is interesting to note that the hollow sphere shell is composed of some small nanoparticles, which makes the surface of shells rougher.

3.4. Photoluminescence properties

The excitation spectra and emission spectra of $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}$ core-shell structure particles and $\text{Y}_2\text{O}_3:\text{Eu}$ hollow spheres are shown in Figs. 5 and 6, respectively.

The monitoring wavelength of the excitation spectra is 611 nm and the excitation wavelength of emission spectra is 254 nm. Note that the luminescent spectra of SiO₂/Y₂O₃:Eu core-shell structure particles and Y₂O₃:Eu hollow spheres are similar. In excitation spectra, the band near 250 nm (248 and 247 nm) is known to be a charge transfer band (CTB) which is an excitation of an electron from oxygen 2*p* state to an Eu³⁺ state [21]. The band below 210 nm (near 204 and 203 nm) is known to be an exciton in the Y₂O₃ host lattice, which is the electron transferred from oxygen 2*p* state to yttrium state [22]. In comparison with bulk sample [23], there is a blue-shift of host excitation and red-shift of CTB. It is believed that the blue-shift is due to the quantum confinement effects and the red-shift is associated with the surface states of the nanoparticles in shells. The same observation was also reported by Zhang [24]. In the emission spectra, the main peak of 611 nm is the red characteristic emission of Y₂O₃:Eu, which corresponds to the ⁵D₀→⁷F₂ electron dipole transition of Eu³⁺, and there are other two peaks corresponding to ⁵D₀→⁷F₀ (near 575 nm), ⁵D₀→⁷F₁ (near 586 nm) transitions of Eu³⁺, in addition, the peaks are all broadened, according to the XRD patterns and TEM observation, the broadened peaks probably come from the nanocrystals of Y₂O₃:Eu shell, indicating a higher disorder of the Eu³⁺ crystalline environment, a larger portion of the Eu³⁺ ions resides near or at the surface of the nanocrystals.

4. Conclusion

The SiO₂/Y₂O₃:Eu core-shell structure and hollow spherical luminescent materials were synthesized using amorphous SiO₂ as a template. The Y₂O₃:Eu shells are linked with silica cores by a Si–O–Y chemical bond. The size of SiO₂/Y₂O₃:Eu core-shell structure is in the range of 140–180 nm, and the thickness of Y₂O₃:Eu hollow spheres is about 20–40 nm. The PL spectra of SiO₂/

Y₂O₃:Eu core-shell materials and Y₂O₃:Eu hollow spheres have better red luminescent properties.

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