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Yidong Li, Liyuan Xiao, Yingliang Liu, Pengfei Ai and Xiaobo Chen

Department of Chemistry, Jinan University, Guangzhou 510632, People’s Republic of China

E-mail: tiuyl@jnu.edu.cn

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Abstract

Nanocrystalline SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ phosphor layers were coated on nonaggregated, monodisperse and spherical SiO$_2$ particles using a hydrothermal homogeneous precipitation. After annealing at 1100 °C, core-shell SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles were obtained. They were characterized with x-ray diffraction (XRD), scanning electron microscopy, transmission electron microscopy and photoluminescence techniques. XRD analysis confirmed the formation of SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles; it indicated that the SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ shells on SiO$_2$ particles consisted of hexagonal crystallites. The core-shell phosphors obtained are well-dispersed submicron spherical particles with a narrow size distribution. The thickness of the coated layer is approximately 20–40 nm. Under ultraviolet excitation (361 nm), the particles emit blue light at about 440 nm due to the Eu$^{2+}$ ions in their shells.

Keywords: SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$, core-shell structure, blue phosphor, hydrothermal homogeneous precipitation method

1. Introduction

Recently, much effort has been devoted to the design and controlled fabrication of nanostructured materials with functional properties. Among them, core-shell particles have attracted much interest because of their unique properties and outstanding performance. Different from single-component materials, the synthesis of core-shell particles has opened new directions for material research [1–3]. Core-shell composites can be monodisperse spherical particles with good optical performance for applications. There are numerous methods of preparing core-shell-structured materials including layer-by-layer self-assembly [1, 4], coprecipitation [5], sol–gel process [6, 7], surface reaction [8] and metalorganic vapor phase epitaxy (MOCVD) [9]. These wet chemical techniques can offer the possibilities of controlling homogeneity, phase purity, size distribution, surface area and microstructure uniformity of the powder.

Novel light emitting diodes (LEDs) have resulted in new requirements for the phosphor materials [10]. The desired properties of the phosphor particles include a perfect spherical shape, narrow size distribution (0.5–2 µm) and absence of agglomeration [11]. Spherical morphology allows achieving high brightness, high spatial resolution, high packing density and low light scattering [12, 13].

The size of silica particles can be controlled from nanometers to micrometers using the Stöber process. These particles are frequently used in core-shell materials either as cores or as shells [8, 14, 15]. If the silica spheres could be coated with phosphor layers then a core-shell phosphor material with spherical morphology would be obtained and the size of the phosphor particles could be controlled by the silica cores. Furthermore, because silica is cheaper than most phosphor materials, which often employ expensive rare-earth elements as activators and/or host components, core-shell phosphor materials should be cheaper than pure phosphors.
SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ is a potential blue phosphor suitable for LEDs and other luminescent devices. It is conventionally prepared in a solid-state reaction at high temperature. However, it is very difficult to control the particle size and crystal structure under these conditions [10, 16]. Hydrothermal homogeneous precipitation is one of the ‘soft’ chemical methods, which was successfully employed to prepare phosphor particles with suitable morphology. This method can work at lower temperatures compared with the solid-state reaction.

In this work, we obtained monodisperse and spherical core-shell SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ phosphors by hydrothermal homogeneous precipitation. The thus produced particles have advantages of low processing temperature, high monodispersity and purity of the product. We characterized the structure, morphology and photoluminescent properties of these core-shell phosphors.

2. Experimental section

The starting materials were tetraethoxysilane (TEOS, 99%, Tianjin Fuchen Chemical Reagent Factory), Al(NO$_3$)$_3$·9H$_2$O (analytical reagent = A.R., Shanghai Zhenxin Reagent Factory), SrCO$_3$ (A.R., Tianjin Fuchen Chemical Reagent Factory), NH$_2$OH (25 wt%, A.R., Guangzhou Chemical Reagent Factory), urea (A.R., Guangzhou Chemical Reagent Factory), HNO$_3$ (A.R., Guangzhou Chemical Reagent Factory), ethanol (A.R., Tianjin Youngda Chemical Reagent Company Ltd) and Eu$_2$O$_3$ (99.99%).

2.1. Synthesis of silica cores

Monodisperse silica spheres of 560 nm size were synthesized by hydrolysis of TEOS in an alcohol medium, in the presence of water and ammonia, with the Stöber [17] process. In a typical experiment, 17.2 ml of TEOS, 36 ml of deionized H$_2$O and 196 ml of NH$_3$·H$_2$O were added into 152 ml of absolute ethanol and stirred at room temperature for 4 h, which produced a white silica colloidal suspension. The silica particles were centrifugally separated from the suspension and washed with ethanol three times. They were then dried at 60 °C for 10 h resulting in silica spheres.

2.2. Synthesis of core-shell structured SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ phosphors

The core-shell SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles were prepared with a hydrothermal homogeneous precipitation method which is schematically illustrated in figure 1. Firstly, Eu$_2$O$_3$ and SrCO$_3$ powders were dissolved in a minimum amount of nitric acid. They were then dried and dissolved in deionized water to form strontium nitrate and europium nitrate solution. Secondly, certain amounts of SiO$_2$ particles were ultrasonically dispersed in the stock solution containing a certain amount of TEOS, 0.1molL$^{-1}$ Al(NO$_3$)$_3$, 0.049 molL$^{-1}$ Sr(NO$_3$)$_2$ and 0.5 molL$^{-1}$ (NH$_4$)$_2$CO. The dispersions were then sealed in a 50 ml Teflon-lined stainless autoclave and maintained at 160 °C for 24 h. After the autoclave was naturally cooled to room temperature, the precipitate was washed with distilled water three times and dried at 160 °C in an air ambient. Then, the samples were heated to 1100 °C at a heating rate of 5 °C min$^{-1}$ and held at this temperature for 2 h in an activated carbon reducing atmosphere.

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out using a Rigaku Model D/max-II B x-ray diffractometer with Cu K$_\alpha1$ (λ = 0.15405 nm) radiation at a 0.02° (2θ) min$^{-1}$ scanning steps. The sample morphology was studied with scanning electron microscopy (SEM, Philips XL-30) and transmission electron microscopy (TEM, Philips TECNAI 10). The particle size and its distribution were evaluated with a nano particle size analyzer (Malvern Zetasizer Nano ZS). Photoluminescence was measured with a HITACHI F-4500 fluorescence spectrophotometer using a Xe lamp as the excitation source.

3. Results and discussion

3.1. XRD analysis

Figure 2 shows the XRD patterns of bare SiO$_2$ particles, SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles and SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ powders, as well as the standard reference data for SrAl$_2$Si$_2$O$_8$ (JCPDS No. 35-0073) as a reference.
(JCPDS No. 35-0073). For bare SiO$_2$ particles, no sharp peaks are observed as shown in figure 2(a) and only a broad feature is seen at $2\theta = 22.0^\circ$, which is characteristic of amorphous SiO$_2$ (JCPDS No. 29-0085). For the SiO$_2$@SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ particles (figure 2(b)), all the diffraction peaks of crystalline SrAl$_2$Si$_2$O$_8$ are present beside the amorphous SiO$_2$ band, suggesting that the coatings of SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ have well crystallized on the surface of amorphous silica particles. This pattern coincides well with that of pure SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ powder (figure 2(c)) and the standard data for SrAl$_2$Si$_2$O$_8$.

3.2. Morphology of the core-shell particles

Figure 3(a) shows an SEM image of bare SiO$_2$ particles. The particles are well separated and spherical with an average size of 560 nm. On the contrary, the SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ powder samples contain aggregates sized between 10 and 100 $\mu$m (figure 3(b)). After being coated by one layer of SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$, the resulting SiO$_2$@SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ particles maintain the morphology of the silica particles. The composite particles are still spherical and non-aggregated, they have rough surfaces and are slightly larger than the bare SiO$_2$ particles owing to the additional layer of SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$. After annealing at 1200 $^\circ$C, the silica spheres have partly collapsed and agglomerated (figure 3(d)).

Figure 4 presents TEM images of silica particles before and after coating with SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$. The surface of the bare SiO$_2$ particles is very smooth (figure 4(a)), and the core-shell structure of the SiO$_2$@SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ particles can be clearly seen because of the different electron absorption in the core and the shell (figure 4(b)). The cores are black spheres with an average diameter of 560 nm, which is similar to the bare SiO$_2$ particles in figure 3(a), whereas the shells have a gray appearance and an average thickness of 20–40 nm.

The average particle sizes and standard deviations of the bare SiO$_2$ and core-shell SiO$_2$@SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ particles are summarized in table 1. After coating one layer of SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ on SiO$_2$ particles, the average particle size increased from 560 to 586 nm with a narrow particle size distribution (figure 5). Compared with the bare SiO$_2$ particles, the standard deviation of the coated samples increased from 5 to 6%. However, the SiO$_2$@SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ particles are still monodisperse and nonaggregated.

3.3. Luminescence properties of SiO$_2$@SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ particles

Figure 6 presents room-temperature photoluminescence excitation and emission spectra of the SiO$_2$@SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ particles and SrAl$_2$Si$_2$O$_8$ : Eu$^{2+}$ powders. Both the excitation and emission bands can be assigned to the well-known Eu$^{2+}$ transitions between the ground state $^8$S$_7/2$(4f$^2$) and the excited states of the 4f$^6$5d$^1$ configuration. The excitation spectra consist of a broad feature between 250 and 400 nm with the maximum at 360 nm (figure 6,
Figure 4. TEM images of the (a) bare SiO$_2$ particles and (b) core-shell SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles annealed at 1100 °C.

Figure 5. Size distribution of the SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles.

spectra (a) and (b)), which is attributed to the charge-transfer band between Eu$^{2+}$ and O$^{2−}$. The UV-excitation of the SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles at room temperature yielded bright blue luminescence peaking at 442 nm (figure 6, spectrum (c)). The spectrum is broad (half-width ~ 100 nm) but symmetric. It indicates one emission mechanism, which can be assigned to Eu$^{2+}$. The luminescence of SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles is slightly weaker than that of the SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ powders, which were also annealed at 1100 °C. It is known that the quantum yield of doped nanoparticles is usually lower than that of the corresponding bulk material because of numerous defects on the nanocrystal surface [18]. The coating of the core-shell particles is so thin (nanometer scale) that it contains numerous surface defects which enhance the non-radiative relaxation.

The sharp Eu$^{2+}$ peaks do not appear in figure 6, which means that the excited state of the 4f$^5$5d configuration is lower in energy than the lowest excited state of the 4f$^7$ configuration in the SrAl$_2$Si$_2$O$_8$ matrix. Furthermore, the characteristic emission peak of Eu$^{3+}$ is not observed. This may be explained by that Eu$^{3+}$ was mostly reduced to Eu$^{2+}$.

4. Conclusions

In this work, a blue phosphorescent material, core-shell SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles, was prepared with a uniform size distribution using a simple hydrothermal homogeneous precipitation process followed by annealing at 1100 °C. The obtained core-shell structured SiO$_2$@SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$ particles maintain spherical morphology and sub-micrometer size. Upon UV excitation, they show luminescence typical of SrAl$_2$Si$_2$O$_8$: Eu$^{2+}$. The photoluminescence excitation and emission spectra reveal that Eu$^{2+}$ did incorporate into SrAl$_2$Si$_2$O$_8$ and maintain its luminescent properties.

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