



Fabrication and Photoluminescence Properties of Monodispersed $\text{SiO}_2@ \text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ Core-Shell Submicron Spheres

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Nanocrystalline $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ phosphor layers were coated on the surface of preformed submicron silica spheres by sol-gel method. The resulted monodispersed $\text{SiO}_2@ \text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell submicron spherical phosphors were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and photoluminescence spectra. The XRD results demonstrated that the $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ layers began to crystallize on the SiO_2 spheres at 900 °C and the crystallinity increased with raising the annealing temperature. The obtained monodispersed core-shell spherical phosphors have perfect spherical shape with narrow size distribution (average size 500 nm). The Eu^{2+} shows a strong photoluminescence (dominated by $4f^65d^1 \rightarrow 4f^7$ red emission at 390 nm) due to an efficient energy transfer from vanadate groups to Eu^{2+} . The photoluminescence intensity of Eu^{2+} increases with raising the annealing temperature.

Keywords: Phosphors, Nanostructures, Sol-gel processes, Optical properties, X-ray diffraction.

INTRODUCTION

In recent years, advanced materials derived from core-shell structure are of extensive scientific and technological interests due to their potential applications in magnetic, mechanical, thermal, electro-optical, electronics, photonics, catalysis, *etc.*¹⁻⁸. The core and shell domains may be composed of a variety of materials including polymers, inorganic solids and metals. For the core-shell structured particles, the structure, size and composition of these particles can be easily altered in a controllable way to tailor their magnetic, optical, mechanical, thermal, electrical, electro-optical and catalytic properties. A number of methods have been employed to synthesize the core-shell materials, for example, sol-gel process, layer-by-layer self-assembly processes, template directed self-assembly, spray pyrolysis, hydrothermal and solvothermal precipitation method⁹⁻¹⁵.

The ideal morphology for phosphor particles includes a perfect spherical shape, narrow size distribution (< 2 μm) and non-agglomeration. Spherical morphology of the phosphors is good for high brightness and high resolution. Additionally, high packing densities and low scattering of light can also be obtained by using spherical phosphors¹⁶. Silica submicron-spheres prepared by Stöber method are the ideal core materials. There are few literatures reported on silica spheres coated with

phosphor layers¹⁶⁻²¹. Silica can be easily made controllably in spherical morphology from nano to micron size²². If the silica spheres are coated with layers of phosphors, a kind of core-shell phosphor materials with spherical morphology will be obtained and the size for the phosphor particles can be controlled by the silica cores. The non-agglomeration, narrow size distribution and perfect spherical shape are the ideal morphology of phosphor particles, which has high packing densities and low scattering of light and is good for improvement of brightness and resolution. The core-shell phosphor materials will be low cost material than the pure phosphor materials in unit mass because silica is low cost than most of the phosphor materials²¹.

It is well known rare earth luminescent materials have considerable applications in many area including fluorescent lighting devices and the display devices, such as tricolor lamps, cathode ray tubes, liquid crystal displays, field emission displays and plasma display panels²³⁻²⁵, *etc.* Eu^{2+} activated $\text{SrAl}_2\text{Si}_2\text{O}_8$ is an important commercial blue phosphor used in color television and the high-pressure mercury lamp^{26,27}. Many effective techniques have been developed to synthesize the phosphors including solid-state reaction^{28,29}, sol-gel³⁰, hydrothermal reaction^{31,32} and reverse microemulsion method³³. To the best of our knowledge, no work has been reported on the fabrication of the monodispersed $\text{SiO}_2@ \text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell

submicrospheres. In this paper, we select $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ as the phosphor shells and silica spheres as the cores, respectively, to obtain the core-shell structured $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ materials *via* the Pechini-type sol-gel process and characterize the structure, morphology and photoluminescent properties of the resulting samples.

EXPERIMENTAL

The highly monodispersed spheres of silica in the size range of 450-500 nm were synthesized by the well-known Stb er process²². This process produces the silica particles with a narrow size distribution in the sub-micrometer range and the particle size depends on relative concentration of the reagent. In the current work, the mixture containing 0.1 mol/L tetraethoxysilane (TEOS (99 wt. %, analytical reagent, A.R.), 1 mol/L H_2O and 7 mol/L NH_4OH (25 wt. %, A.R.) was stirred at room temperature for 4 h, resulting in the formation of white silica colloidal suspension. The silica particles were centrifugally separated from the suspension and washed with ethanol three times.

SiO_2 core- $\text{Sr}_{0.99}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}_{0.01}$ shell monodispersed spherical particles ($\text{SiO}_2@\text{Sr}_{0.99}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}_{0.01}$) were synthesized by a Pechini sol-gel process. Appropriate amounts of $\text{Eu}(\text{OOCCH}_3)_3 \cdot 2\text{H}_2\text{O}$ (99 %) and citric acid were dissolved in ethanol and H_2O solution mixture in volume ratio ethanol/ H_2O = 7:1. Subsequently, the solution was stirred with dropping 2 mL HNO_3 as catalyst. Then citric acid as chelating agent for metal ions was added to the above solution. The molar ratio of citric acid to metal ions was 2:1. Furthermore, the silica particles were added into the solution until transparent sol was obtained. The silica particles were obtained by centrifugation. The resultant gel was dried at 140 °C for 2 h immediately and then preheated at 500 °C for 3 h. Finally, the preheated particles were annealed to 800-1000 °C and held there for 2 h. In this method, the monodispersed $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell spherical particles were synthesized.

The morphology and microstructure of the were observed by using a transmission electron microscopy (TEM, Hitachi H-800) and a field-emission scanning electron microscopy (FESEM, Hitachi S-4700). X-ray diffraction (XRD) spectra were carried out with D/Max2500VB2 + PC diffraction apparatus. The photoluminescence was measured using a Hitachi F4600 fluorescentometer and energy correction was conducted for the spectrum data collection.

RESULTS AND DISCUSSION

Fig. 1 shows the FESEM images of the as-prepared SiO_2 spheres (a), 1100 °C annealed $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ powders (b), monodispersed $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell submicron spherical phosphors annealed at different temperatures 900 °C (c), 1000 °C (d) and 1100 °C (e), respectively. Fig. 1 showed that the as-prepared SiO_2 consists of spherical particles with a uniform particle size of about 500 nm and these particles are non-aggregated with narrow size distribution. While for the pure $\text{SrAlSiO}_4:\text{Eu}^{2+}$ powders (Fig. 1 b), irregular particles with size distribution from 200 to 900 nm are observed. After functionalizing the silica spherical particles by $\text{SrAlSiO}_4:\text{Eu}^{2+}$ coatings, the resulting $\text{SiO}_2@\text{SrAlSiO}_4:\text{Eu}^{2+}$ particles still keep

the morphological properties of the silica particles, such as the spherical morphology, non-aggregation and uniform size distribution, but slightly larger than the pure silica particles due to the additional layers of $\text{SrAlSiO}_4:\text{Eu}^{2+}$ on them [Fig. 1 (c), (d) and (e)]. However, it should be mentioned that the FESEM images can only provide the basic information on the morphology of $\text{SiO}_2@\text{SrAlSiO}_4:\text{Eu}^{2+}$ particles in the large scale (namely, all of the SiO_2 particles remain spherical and nonaggregated after being subjected to the sol-gel coating of $\text{SrAlSiO}_4:\text{Eu}^{2+}$ layers on them) and the core-shell structure of $\text{SiO}_2@\text{SrAlSiO}_4:\text{Eu}^{2+}$ particles cannot be resolved from the FESEM images due to the low magnification.

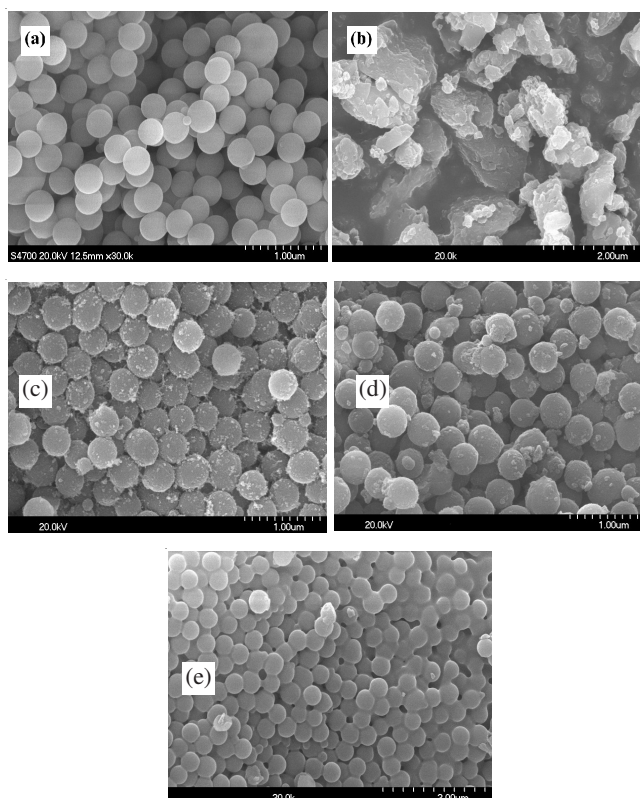


Fig. 1. FESEM images of the as-prepared SiO_2 spheres (a), 1100 °C annealed $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ powders (b), monodispersed $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell submicron spherical phosphors annealed at different temperatures 900 °C (c), 1000 °C (d) and 1100 °C (e), respectively

The representative TEM images of the as-prepared SiO_2 spheres (a) and the core-shell structured $\text{SiO}_2@\text{SrAlSiO}_4:\text{Eu}^{2+}$ spherical phosphors annealed at 900 °C (b), 1000 °C (c) and 1100 °C (d) are depicted in Fig. 2 respectively. For the $\text{SiO}_2@\text{SrAlSiO}_4:\text{Eu}^{2+}$ spherical particles, the core-shell structure can be seen clearly due to the different electron penetrability for the cores and shells. The cores are black spheres with an average size of about 500 nm, which is similar to those of the pure SiO_2 particles [Fig. 2 (a)] and the shell shows gray color with an average thickness of 30 nm, but the thickness of the coating is not uniform, especially in Fig. 2 (d).

Fig. 3 shows the XRD patterns of the as-prepared SiO_2 spherical particles (a), core-shell $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ spherical phosphors annealed at 900 °C (b), 1100 °C (c) and 1100 °C (d), pure $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ phosphors annealed at

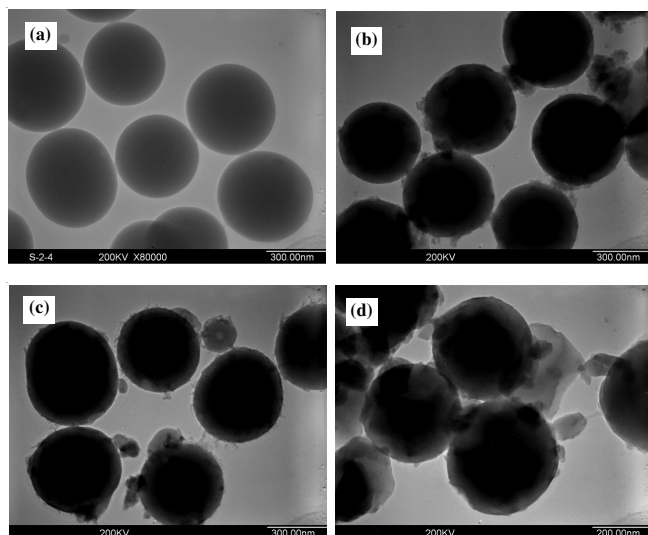


Fig. 2. TEM images of the as-prepared SiO_2 spheres (a), core-shell structured $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ spherical phosphors annealed at 900 °C (b), 1000 °C (c) and 1100 °C (d)

1100 °C (e) as well as the JCPDS card (No. 35-0073) for $\text{SrAl}_2\text{Si}_2\text{O}_8$ as a reference, respectively. For SiO_2 particles, no diffraction peak is observed except for a broad band centered at $2\theta = 22^\circ$, which is the characteristic peak for amorphous SiO_2 (JCPDS 29-0085). For the core-shell $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ spherical phosphors annealed at 1100 °C [Fig. 3 (d)], besides the broad band at $2\theta = 22^\circ$ from amorphous SiO_2 , most of the diffraction peaks belonging to crystalline $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ are present, suggesting that the coatings of $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ have crystallized well on the surfaces of amorphous silica particles. This is in good agreement with the situation for the pure $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ phosphors annealed at 1100 °C. The intensity of the diffraction peaks of core-shell $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ spherical phosphors increase with the temperature increasing due to the improvement of crystallinity.

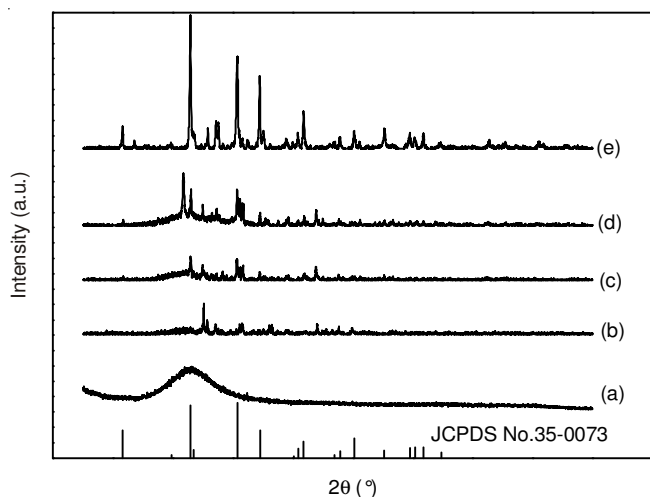


Fig. 3. XRD patterns of the as-prepared SiO_2 spherical particles (a), core-shell $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ spherical phosphors annealed at 900 °C (b), 1100 °C (c) and 1100 °C (d), pure $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ phosphors annealed at 1100 °C (e)

Figs. 4 and 5 show the excitation and emission spectra of monodispersed $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell spherical

phosphors. The excitation spectra (Fig. 4) were obtained by monitoring the emission of Eu^{2+} at 390 nm. It can be seen clearly that the excitation spectrum consists of a strong and broad band with a maximum at about 311 nm. This can be attributed to the charge transfer from Eu^{2+} to O^{2-} . Under 311 nm light excitation, the annealed $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell phosphors show blue emission. The emission spectra (Fig. 5) contains exclusively the characteristic transition lines of Eu^{2+} , which is dominated by the hypersensitive blue emission $4f^65d^1 \rightarrow 4f^7$ transition at 390 nm. The general $f-f$ transition lines of Eu^{3+} in the longer wavelength region have not been observed due to their relatively weak intensity or the reduction from Eu^{2+} to Eu^{3+} . Effect of annealing temperature on the photoluminescence emission intensity of the Eu^{2+} in $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell spherical phosphors is shown in Fig. 5. Obviously, the photoluminescence intensities all increase with increasing annealing temperature. This can be attributed to the enhanced crystallinity of the $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell spherical phosphors.

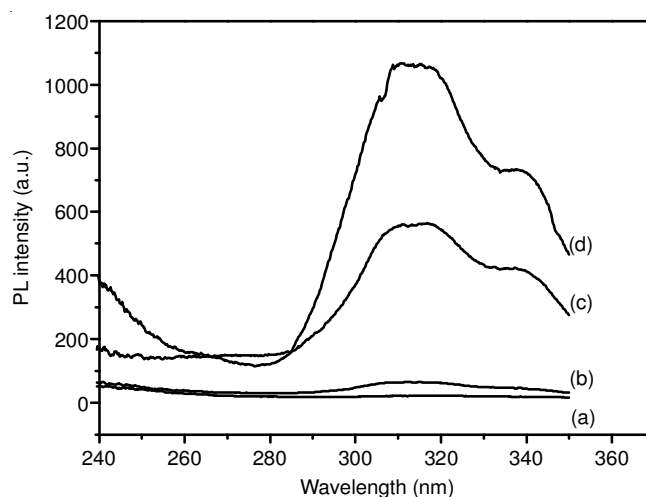


Fig. 4. Excitation spectra of the $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell phosphors annealed at different temperatures 900 °C (a), 1000 °C (b), 1100 °C (c), and $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ phosphors annealed at 1100 °C (d)

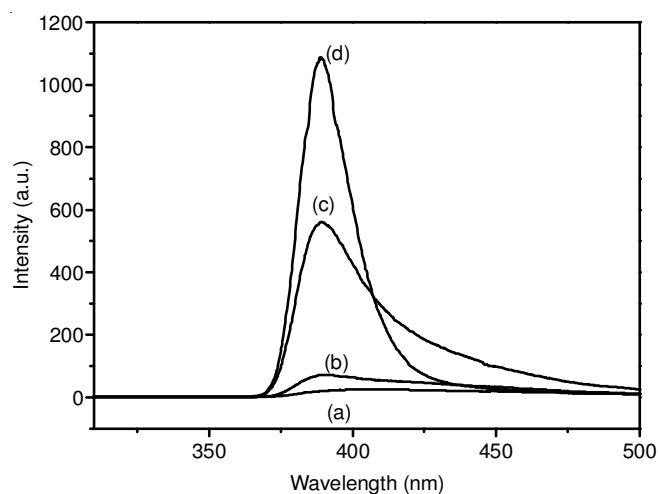


Fig. 5. Emission spectra of the $\text{SiO}_2@\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ core-shell phosphors annealed at different temperatures 900 °C (a), 1000 °C (b) and 1100 °C (c), and $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ phosphors annealed at 1100 °C (d)

Conclusion

Monodispersed SiO₂@SrAl₂Si₂O₈:Eu²⁺ core-shell submicron spherical phosphors with uniform size distribution have been successfully prepared by sol-gel method followed by annealing at different temperature. Upon UV excitation, the luminescence properties of the SiO₂@SrAlSiO₄:Eu²⁺ core-shell spherical phosphors are typical those of shell components, SrAlSiO₄:Eu²⁺. The photoluminescence intensity of the SiO₂@SrAlSiO₄:Eu²⁺ core-shell spherical phosphors can be tuned by the annealing temperatures. The advantages of the core-shell spherical phosphors prepared by this process are the easy availability of homogeneous spherical morphology in different size and its wide applicability for other phosphor materials.

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