

Synthesis silica sphere and core-shell $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}@\text{SiO}_2$ phosphor nanoparticles by sol-gel method

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ABSTRACT

The well-dispersion and nano-scale of silica sphere were synthesized through sol-gel process by using TEOS as the precursor at room temperature. We also can control the sphere size with the diameter 60 nm, 180 nm and 300 nm. The size distribution of silica sphere is examined via a photo correlation spectroscopy. Furthermore $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film 10 nm in thickness were coated onto silica spheres using the sol-gel method. Uniform core-shell phosphor particles were observed using FE-SEM. The XRD and HR-TEM results indicated that the coated-shell layer was well crystallized after sintering at 1000 °C. The $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}@\text{SiO}_2$ PL measurement showed a red-emission at the main 615 nm wavelength.

Keywords: nano-scale sol-gel process red-emission

1 INTRODUCTION

The preparation of monodisperse nanoparticles with uniform shapes and size has been of growing interest due to the utilization for various types of functional application fields, such as electric, optical and chemical devices. Although there have been a large number of techniques for preparing monodisperse particles, the uniformity in shape and size has not been satisfied in most techniques [1]. In recent years, advanced materials device from core-shell composition particles are of extensive scientific and technological interests due to the ability to fine tune their properties [2-3]. Core-shell materials consist of a core structural domain covered by a shell domain. The core and shell domains may be composed of a variety of materials including polymers, inorganic solids and metals. Core-shell materials can also be used protect medicines or other materials from dissolution or hydrolysis [4] and to strengthen polymeric materials [5]. Therefore, many synthesis method have been developed to fabricate such core-shell materials such as sol-gel process [6], template-directed self-assembly [7] and encapsulation of silica nanoparticles by in situ polymerization [8].

Furthermore, the current demand for high-resolution for high-resolution and increased efficiency in phosphors for cathode ray tubes (CRT) [9], plasma display panel (PDP) [10] and field emission displays (FED) [11] has promoted the development of phosphors that perform at decrease of particles size. The ideal morphology of phosphor particles includes a perfect spherical shape ($< 1 \mu\text{m}$) [12], narrow size distribution, and nonagglomeration. Spherical

morphology of the phosphors is good for high brightness and high resolution.

In this study, we used TEOS as the precursor to synthesize the nano-scale of silica sphere by sol-gel process at room temperature. We think that the use nano-scale of silica sphere as the core-shell phosphors template has at least the following advantages: (a) the size of silica powder was between 250 nm ~ 200 nm, which fitted narrow size distribution (b) the size and amount of silica can be controlled easily. (c) well dispersion exist in solution. Scanning electron microscopy (SEM), Transition electron microscopy (TEM) and X-ray diffraction analysis (XRD) were employed to identify and understand the morphology of the synthesized material while photo- luminance analysis was employed to realize the excitation and emitting properties of phosphors.

2 EXPERIMENTAL

2.1 Synthesis of materials

The amorphous sub-micrometer silica spheres were prepared by sol-gel synthesis method. Tetraethoxysilane (TEOS, 99 wt %) was firstly mixed with ethanol (95 wt %) with the solution stirred for 10 min. the ammonia hydrate (28 wt %) aqueous solution was added into a tetraethoxysilane / ethanol solution gradually at a rate of 0.01 ml/sec for 10 minutes. The solution was continuously stirred at room temperature. The different silica spheres size was formed by different ration of TEOS/ NH_3OH . The ratio of TEOS/ NH_3OH was 2:1, 1:1, and 1:2 respectively. The synthesized silica spheres were used for a phosphor coating process. The synthesis procedure of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}@\text{SiO}_2$ also by sol-gel method was as follows: 0.75 M gadolinium chloride and 0.17 M europium chloride were added directly to the silica sphere solution at a stirring speed of 300 rpm. The gadolinium chloride and europium chloride were then dissolved slowly by adding 0.01 M NaOH aqueous solution gradually at a rate of 1 ml/ min for 2 hours to keep the pH value between 10 ~ 11. The condensed powders were collected and dried at room temperature prior to washing using D.I. water two times. The powder was then sintered at 1000 °C in the air for 5 hours. Approximately $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}@\text{SiO}_2$ core-shell phosphors were obtained.

2.2 Characterizations of the phosphor

The size of the silica spheres was examined using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The feature, and crystallization of core-shell phosphors were obtained using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800), high-resolution transmission electron microscopy (HR-TEM, JEOL JEM 2010 and X-ray powder diffraction technique using a Cu target ($\text{CuK}\alpha = 1.5418 \text{ \AA}$, RIGAKU Miniflex). For the photo-luminescent analysis, the excitation and emission spectra of particles were measured using a fluorescence spectrophotometer (Hitachi F-4500) using a Xe lamp (150 W) as the excitation source. The wavelength range in the fluorescence spectrophotometer was from 200 ~ 1100 nm and the scanning rate set for 1 nm/s. All of these measurements were performed at room temperature.

3 RESULTS AND DISCUSSIONS

3.1 Size distribution analysis of bare silica spherical particles.

Figure 1(a), 1(b) and 1(c) shows the feature and the size of silica particles using FE-SEM. The synthesized SiO_2 particles were found spherical with a very uniform size in the range of 60 nm, 170 nm and 250 nm by different TEOS/ NH_3OH molar ratio. The electron diffraction pattern reveals that the silica spheres were amorphous phase.

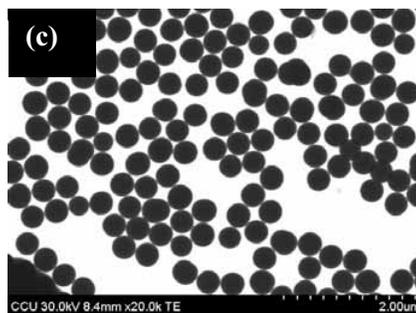
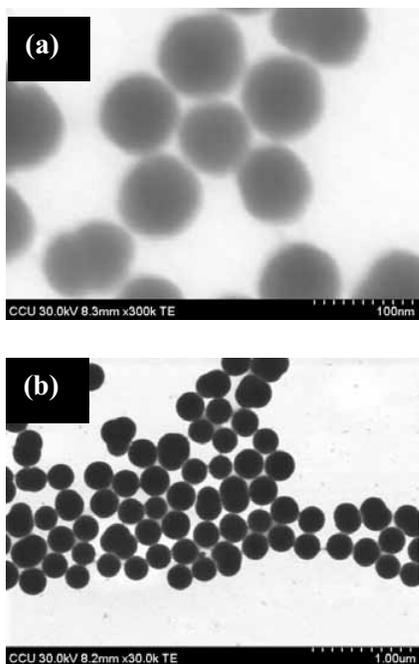


Figure 1. FE-SEM images of different particle size. (a) 60 nm (b) 150 nm and (c) 250 nm.

3.2 Characterizations of coated shell phosphors of $\text{Gd}_2\text{O}_3: \text{Eu}^{3+} @ \text{SiO}_2$

We used the 250 nm of silica sphere to be the core-shell phosphor template by sol-gel method. Figure 2(a) shows the FE-SEM image of $\text{Gd}_2\text{O}_3: \text{Eu}^{3+} @ \text{SiO}_2$ particles. The particle sizes of $\text{Gd}_2\text{O}_3: \text{Eu}^{3+} @ \text{SiO}_2$ was about 250 nm and the particle surface was very smooth. Figure 2(b) shows the backscattering electron (BSE) image of the $\text{Gd}_2\text{O}_3: \text{Eu}^{3+} @ \text{SiO}_2$. The image demonstrates a clear brightness contrast between the shell layers and core particles. The contrast indicates the different element materials in the shells and particles.

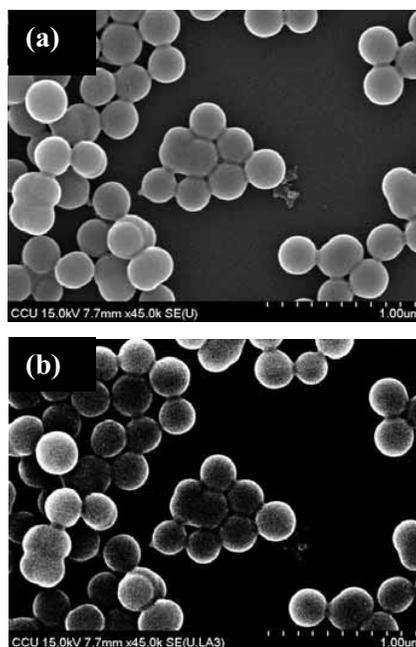


Figure 2. (a) SEM photograph of $\text{Gd}_2\text{O}_3: \text{Eu}^{3+}$ coated on the surface of silica particles and (b) BSE-SEM photograph.

As a result, we believe that the various compounds covered the silica sphere surface in a thin layer of phosphors. Figure 3 shows the X-ray powder diffraction patterns of the (a) coated material calcinated at 1000 °C, (b) bare silica sphere. There are four main peaks observed clearly and presented in the XRD pattern of the $Gd_2O_3:Eu^{3+}@SiO_2$ material. The diffraction peaks are at $2\theta \approx 28.56^\circ$ (2 2 2), $2\theta \approx 33.10^\circ$ (4 0 0), $2\theta \approx 47.51^\circ$ (4 4 0), and $2\theta \approx 56.40^\circ$ (6 2 2). As a consequence, it is clear that Gd_2O_3 was formed on the silica sphere surface.

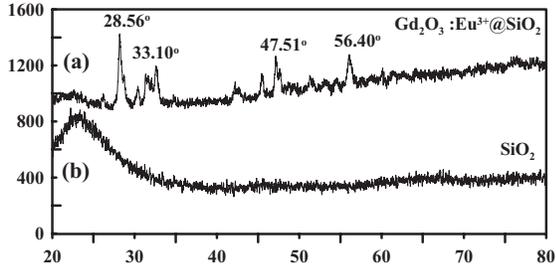


Figure 3. XRD patterns of (a) $Gd_2O_3:Eu^{3+}@SiO_2$, (b) SiO_2 particles.

A further examination of $Gd_2O_3:Eu^{3+}@SiO_2$ particles were carried out using HR-TEM. Figures 3(a), 4(b) represent the sphere features and the electron diffraction pattern of the thin layer, respectively. The results show a good crystalline structure in the outer thin layer.

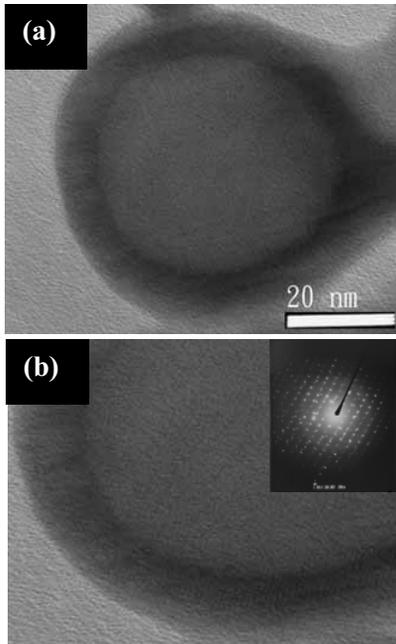


Figure 4. HR-TEM photographs of (a) $Gd_2O_3:Eu^{3+}@SiO_2$ particle (b) crystalline structure of $Gd_2O_3:Eu^{3+}$ and electron diffraction pattern of $Gd_2O_3:Eu^{3+}$.

3.3 Photo-luminescent properties of $Gd_2O_3:Eu^{3+}@SiO_2$.

The excitation spectra and the emission spectra of $Gd_2O_3:Eu^{3+}@SiO_2$ were measured by PL spectrum shown in Fig. 5(a) and 5(b), respectively. The excitation spectra of the red fluorescence ($\lambda = 611$ nm) show a peak at 250 nm, which is attributed to transition towards the charge-transfer state (CTS) due to Eu-O interaction [13]. The Eu – O interaction is the excitation from the ground state of the $4f$ levels to a Eu-O charge transfer state. In the coated particle spectra, the weak broad (dash line) observed in 310 nm is related to Gd^{3+} transitions, which is due to $Gd^{3+} \rightarrow Eu^{3+}$ energy transfer. The peaks near 350 nm and 475 nm can be assigned to the higher energy level ($f-f$) transitions of Eu^{3+} [13]. The emission spectra in Fig 5 (b) show the strongest emission peak near 611 nm $Gd_2O_3:Eu^{3+}@SiO_2$. This peak corresponds to a forced electron dipole transition of Eu^{3+} ($^5D_0 \rightarrow ^7F_2$) that is allowed only when europium is occupied in low symmetries. As a consequence, the core-shell material still exhibits the same luminescent properties as bulk materials. We found other energy transition peaks for Eu^{3+} corresponding to $^5D_0 \rightarrow ^7F_2$ (near 625 nm), $^5D_0 \rightarrow ^7F_3$ (near 650 nm) and $^5D_0 \rightarrow ^7F_4$ (near 705 nm).

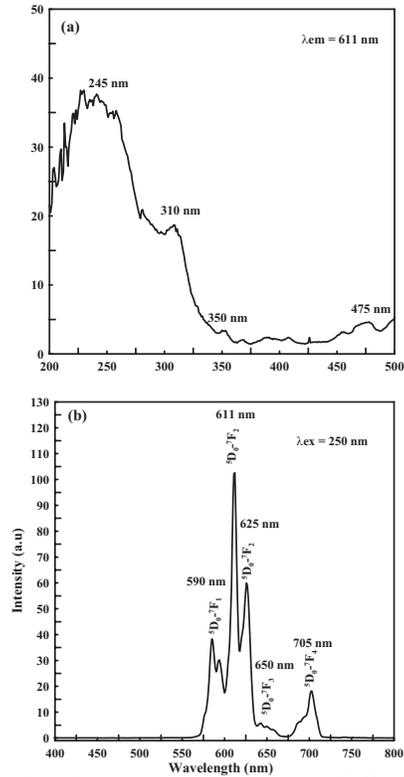


Figure 5. (a) The excitation spectrum of $Gd_2O_3:Eu^{3+}@SiO_2$ phosphor and (b) emission spectra of $Gd_2O_3:Eu^{3+}@SiO_2$ phosphors

4 CONCLUSION

In this study, we presented a very simple method to prepare different size of silica spheres via 60 nm, 150 nm and 250 nm and synthesize $\text{Gd}_2\text{O}_3: \text{Eu}^{3+}@\text{SiO}_2$ powder. The $\text{Gd}_2\text{O}_3: \text{Eu}^{3+}@\text{SiO}_2$ materials remain the red-emission luminescent properties by PL measurement. The core-shell phosphors maintained the same emission ability as the bulk materials and the novel core-shell phosphors possessed great potential in quantum phosphor applications.

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