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Synthesis and characterization of monodispersed $BaSO_4/Y_2O_3:Eu^{3+}$ core–shell submicrospheres

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ABSTRACT

Spherical $BaSO_4$ particles have been coated with $Y_2O_3:Eu^{3+}$ phosphor layers ($BaSO_4/Y_2O_3:Eu^{3+}$) by the wet chemical method. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dipersive spectroscopy (EDS), photoluminescence spectra were utilized to characterize the $BaSO_4/Y_2O_3:Eu^{3+}$ core–shell-structured phosphor particles. The obtained core–shell phosphors consist of well dispersed submicron spherical particles with narrow size distribution. XRD result shows that no reaction occurred between the $BaSO_4$ cores and the $Y_2O_3:Eu^{3+}$ shells even after annealing at 1400 °C. TEM and EDS results show that $BaSO_4$ particles are well coated with the shell of $Y_2O_3:Eu^{3+}$. The $BaSO_4/Y_2O_3:Eu^{3+}$ core–shell particles show a red emission corresponding to $^5D_0—^7F_2$ of Eu^{3+} under the excitation of ultraviolet.

1. Introduction

Rare earth luminescent materials have considerable applications in almost any devices involving fluorescent lighting devices and the display devices, such as tricolor lamps, cathode ray tubes (CRTs), liquid crystal displays (LCDs), field emission displays (FEDs), and plasma display panels (PDPs), etc [1–4]. Among them, Europium-doped yttrium oxide ($Y_2O_3:Eu^{3+}$) fulfills all the requirements for a good red-emitting phosphor because of its excellent luminescence efficiency, color purity and stability. It can be easily excited by 254 nm from mercury radiation and its sharp emission is located at 613 nm and all other emission lines are weak [5]. However, the prices of rare earth oxides are very expensive and this has limited their applications to a great extent.

In recent years, tremendous effort has been devoted to the design and controlled fabrication of nanostructured materials with functional properties. Among them, surface modification, i.e., the fabrication of core–shell structure, has been attracting much attention due to the ability to fine-tune their properties. Coating the particles with a thin shell of a compatible material makes it possible to improve functional properties and expand a broader range of potential application. The structure, size, and composition of these particles can be altered easily in a controllable way to tailor their magnetic, optical, mechanical, thermal, electrical, electrooptical, or catalytic properties [6,7]. Very recently, this strategy has been extended to the inorganic luminescent systems [8–12]. Examples of such core–shell structures are $Y_2O_3:Eu/Y_2O_3$ [13], (La,Tb 20%)$PO_4 \cdot xH_2O/CePO_4 \cdot xH_2O$ [14]. Results indicated that the formation of core–shell structure is an effective way to decrease the cost of the rare-earth-doped inorganic luminescent systems.

Silica is frequently used in core–shell structured materials [15–18]. Typically, the monodisperse spheres of silica were synthesized by the well-known Stober process, in which TEOS, water and ammonia were used as reagents and absolute ethanol as reaction medium. The cost was increased.

Recently, the monodispersed spherical particles of barium sulfate were successfully synthesized by precipitation method, in which $BaCl_2$, Na_2SO_4 and EDTA were used as reagents. The size and morphology of the obtained $BaSO_4$ particles can be controlled during the process. Barite submicrospheres prepared by this method are the ideal core materials because of their inexpensiveness, non-toxicity, stableness (melting point 1580 °C), chemical inertness, easiness to get spherical particles with narrow size distribution. Moreover, barium sulfate has also been used as the host material in the field of thermoluminescence(TL) [19]. If the barium sulfate spheres are coated with phosphor layers, a kind of core–shell phosphor material with spherical morphology will be obtained, and the size of the phosphor particles can be controlled by the barite core and the number of coating cycles. Furthermore, because barite is cheaper than most phosphor materials, which often employ expensive rare-earth elements as the activators and/or host components, core–shell phosphor materials will be cheaper than pure phosphor materials to some degree.

In this paper, we, for the first time, reported a new monodispersed $BaSO_4/Y_2O_3:Eu^{3+}$ core–shell submicrospheres through coprecipitation method, which was easy to scale up. By controlling the hydrolysis of urea, the obtained particles had spherical, monodispersed morphology and uniform shell thickness. The resulting photoluminescence properties,

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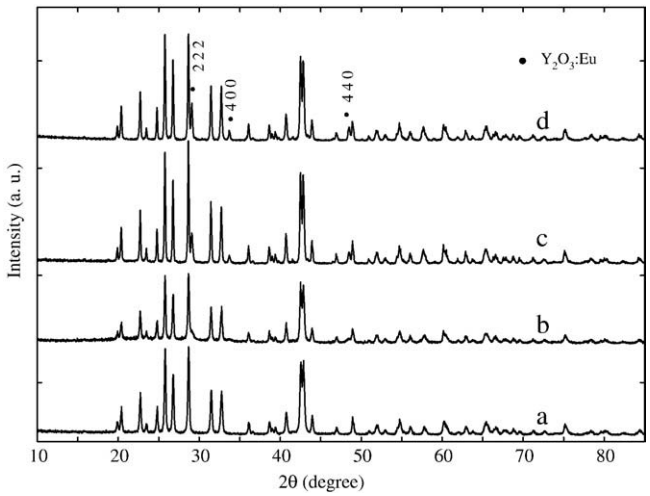

Fig. 1. XRD patterns of the precursor (a) and $BaSO_4/Y_2O_3:Eu^{3+}$ core–shell particles annealed at 800 °C (b), 1200 °C (c), and 1400 °C (d). (·) denoted the cubic phase of Y_2O_3.

core–shell structure and morphology of obtained products were presented.

2. Experimental

2.1. Materials

Sodium sulfate(Na_2SO_4), barium chloride ($BaCl_2 \cdot 2H_2O$), ammonium hydroxide (NH_4OH), disodium ethylenediamine tetraacetate (EDTA-2Na), yttrium oxide (Y_2O_3, 99.99%), europium oxide (Eu_2O_3, 99.999%), and urea ($(NH_2)_2CO$) were all analytical reagent grade.

2.2. Preparation of barium sulfate spheres cores

The synthesis of highly monodispersed submicron $BaSO_4$ spheres was carried out counting with the presence of EDTA. 24.4 g of $BaCl_2 \cdot 2H_2O$ and 37.2 g of disodium ethylenediamine tetraacetate (EDTA-2Na) were mixed in 200 ml of distilled water. The pH of solution was adjusted to 9 by using NH_4OH. Then, 200 ml of 0.5 mol L^{-1} Na_2SO_4 was added to the above liquid under vigorous stirring by using a magnetic stirrer, and after several minutes, a white precipitate formed. The mixture was stirred for another 1 h, and then the solution was

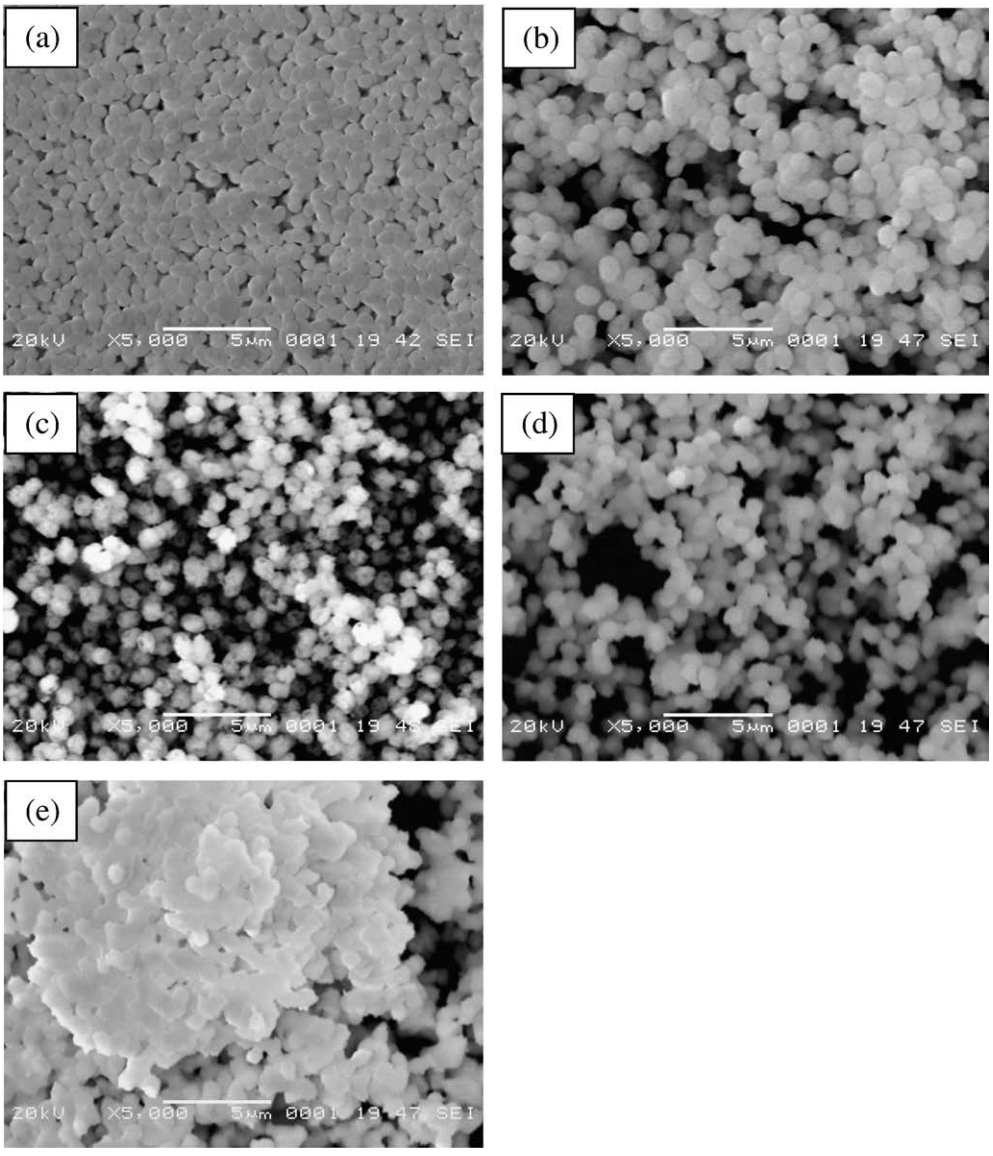

Fig. 2. SEM photographs of the as-formed $BaSO_4$ (a), the precursor (b) and the $BaSO_4/Y_2O_3:Eu^{3+}$ core–shell particles annealed at the 1000 °C(c), 1200 °C (d), and 1400 °C (e).