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Synthesis of the uniform hollow spherical $Sr_2SiO_4:Eu^{2+}$ phosphors *via* an *h*-BN protective method

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ABSTRACT

The uniform hollow spherical $Sr_2SiO_4:Eu^{2+}$ green emitting phosphors have been successfully synthesized using hollow silica spheres as templates by an *h*-BN protective method. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results directly confirmed the existence of the hollow spherical structure with a narrow size distribution and a shell thickness of 15–25 nm. The *h*-BN protective film, observed by high resolution TEM, plays an important role in the formation of the hollow spherical morphology and the improvement of photoluminescence properties. Comparing with the $Sr_2SiO_4:Eu^{2+}$ micron-phosphor prepared by the traditional solid state reaction method, the hollow spherical phosphor with nano-sized grains exhibits stronger green emission under ultraviolet–blue light excitation. This could be attributed to the elimination of surface defects by the *h*-BN coating. This research gives an economic and convenient way to synthesize uniform spherical phosphors with high quantum efficiency.

1. Introduction

White light-emitting diodes (WLEDs) have attracted much more attention as light sources for new generation luminescent and displaying devices due to their high quantum efficiency, low energy consumption, long life time and environmental friendly.[1–4] There are many methods to generate white light, however, the combination of LED chips with phosphors is considered to be the most convenient and economic way [5,6].

The phosphor powders should be dispersed in the resin and dropped on the surface of the LED chip to obtain a uniform phosphor layer, so their morphology and particle size distribution play important roles in improving quality of the WLEDs. Spherical phosphors with a narrow size distribution are getting much more attentions in recent decades [7–11]. However, It is very difficult to achieve that, because most of the potential phosphors, such as silicate and oxynitride, are often synthesized at high temperature with long calcination time, resulting in a significant agglomeration and broad size distribution of the particles [12,13]. A lot of attempts have been made to prepare small phosphor particles with narrow size distribution. Some phosphors are successfully fabricated, such as $SiO_2@YBO_3:Eu^{3+}$ [14], BHA (or BAM) [15] and hollow $Gd_2O_3:Ln$ (Ln = Eu^{3+}, Sm^{3+}) [16] phosphors. We have successfully invented an *h*-BN protective method to synthesize the core–shell structured spherical oxynitride phosphors at relative low temperature, such as $SrSi_2O_2N_2:Eu^{2+}$ and $Sr_2Si_5N_8:Eu^{2+}$ phosphors [17,18].

Due to their unique structural, optical, and surface properties, hollow inorganic spheres have many potential applications, such as catalysis, encapsulation, coatings and drug delivery. For phosphor application, the hollow structure could reduce the usage of the raw materials and eliminate the cost in commercial production, because only the surface of phosphor has contribution to the photoluminescence. Many efforts have also been made towards the fabrication of the hollow spherical phosphors [19–22], however, there is still a challenge to find a simple method.

In this letter, we success in synthesizing hollow $Sr_2SiO_4:Eu^{2+}$ spherical phosphors by the *h*-BN protective method using hollow SiO_2 spheres as templates. The as-received phosphors show an intense green emission under UV excitation.

2. Experimental

2.1. Materials

All the as-received materials are directly used without further purification, which contains $Sr(NO_3)_2$ (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China, >99.99%), Eu_2O_3 (99.99%), ammonium hydroxide (NH_4OH, 25–28%) tetraethyl orthosilicate (TEOS, 99.99%), dilute nitric acid (HNO_3, Analytical reagent, AR), styrene ($C_6H_5CH{=}CH_2$, AR), polyvinylpyrrolidone K-30 (PVP K-30,

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99.99%), ethanol (C_2H_5OH, AR), azo dibutyl cyanide (AIBN, AR), citric acid (C_6H_8O, AR), H_3BO_3 (AR) and polyethylene glycol(PEG, molecular weight = 10,000, AR) and distilled water.

2.2. Preparation of polystyrene (PS) microspheres

The micrometer PS particles with an average diameter of ~800 nm were synthesized by the polycondensation of styrene ($C_6H_5CH{=}CH_2$) via the sol–gel procedure [23]. In a typical procedure, 2.0 g PVP K-30 were added to a 330 ml water–ethanol (V/V = 1:10) solution and stirred at room temperature to make the PVP K-30 completely dissolved in the solution, then 0.3 g AIBN was dissolved in the mixture solution, at last, 33 ml styrene were dissolved in the solution and stirred at 70 °C oil bath with reflux condensation process under N_2 flow for 24 h. The resulting PS spheres were centrifugally separated from the suspension, washed three times with ethanol and dried at 60 °C for 12 h.

2.3. Coating of PS spheres with a SiO_2 shell

The PS spheres were successfully coated with SiO_2 layers on the surface by the basic hydrolysis and condensation of TEOS through the well-know stöber method [24,25]. First, 0.5 obtained PS spheres were added in 200 ml ethanol solution and ultrasonic dispersed for 15 min, then 3 ml TEOS and 8 ml NH_4OH were added in the suspension solution and stirred for another 12 h at room temperature, resulting in the formation of the PS@SiO_2 core–shell structured particles. The PS@SiO_2 particles were centrifugally separated from the suspension, washed three times with ethanol and dried at 100 °C.

2.4. Fabrication of hollow spherical SiO_2@$SrCO_3$:Eu^{3+} core–shell structured precursor particles

The Sr^{2+} and Eu^{3+} ions are coated on the surface of the core–shell structured PS@SiO_2 particles via the famous Pechini-type sol–gel method [26-28]. First, the $Sr(NO_3)_2$ and Eu_2O_3 powders were dissolved in dilute HNO_3 solution to form the Sr^{2+} and Eu^{3+} ion solution. The molar ratio of Eu^{3+} to Sr^{2+} was set to 0.02, which is consistent with the optimum concentration of the Sr_2SiO_4:Eu^{2+} phosphors [29,30]. Then stoichiometric amount of $Sr(NO_3)_2$ and $Eu(NO_3)_3$ solution were dissolved in a water–ethanol (V/V = 1:4) solution with citric acid as chelating agent for metal ions, and the molar ratio of metal ions to citric acid was 1:2. Then the polyethylene glycol (PEG, molecular weight = 10,000) was added with a concentration of 0.10 g/mL. The solution was stirred for 4 h at room temperature. At last, the particles were separated by centrifugation and washed three times with ethanol solution and dried at 100 °C. The obtained PS@SiO_2@$SrCO_3$:Eu^{3+} core–shell structured particles (For convenience, the metal compounds of Sr and Eu elements on the surface of PS@SiO_2 particles are named with @$SrCO_3$:Eu^{3+}.) were annealed at 500 °C for 2 h in air to remove the PS cores and make the outer $SrCO_3$:Eu^{3+} layer adhere tightly to the inner spherical SiO_2 cores.

2.5. Synthesis of the hollow spherical Sr_2SiO_4:Eu^{2+} phosphors via gas reduction and nitridation method

The H_3BO_3 layers were coated on the spherical hollow spheres using the wet chemical method, according to its different solubilities in aqueous solution at different temperatures. The as-prepared hollow spherical and an appropriate amount of H_3BO_3 powders are mixed in distilled water solutions at a relative high temperature. After the H_3BO_3 powders are completely dissolved in distilled water, the solution was naturally cooled to room temperature to make the H_3BO_3 powders coat on the surface of the hollow spherical SiO_2@$SrCO_3$:Eu^{2+} precursor particles.

The obtained hollow spherical SiO_2@$SrCO_3$:Eu^{2+}@H_3BO_3 precursor particles were placed in a boron nitride (BN) boat, and horizontally loaded into the alumina (Al_2O_3) tubular furnace with an inner diameter of 50 mm. The temperature was heated to 1000 °C in 3 h and maintained at 1000 °C for another 2 h, then increased to 1400 °C and kept at the temperature for 8 h in flowing N_2/NH_3 atmosphere. After the heating process, the sample were slowly cooled to 800 °C, then naturally cooled to room temperature. The detailed schematic fabrication procedure of the hollow spherical Sr_2SiO_4:Eu^{2+} phosphors are shown in Scheme 1. For comparison, the pure Sr_2SiO_4:Eu^{2+} phosphors were also synthesized by a traditional solid state reaction method at the same condition expect for the H_3BO_3 coating powders.

2.6. Characterization

All the powder products were well grounded and identified by X-ray powder diffraction (XRD, PW 1700, Philips, Netherlands) using Cu Kα1 radiation (λ = 1.54056 Å) at 40 kV and 100 mA with a graphite monochromator. The powders were placed in a silica chip vertically in the machines with a $2\theta/\theta$ scan axis. The data were collected using a step size of 0.0167° in the 2θ range from 10° to 70° at a scanning speed of 2°/min.

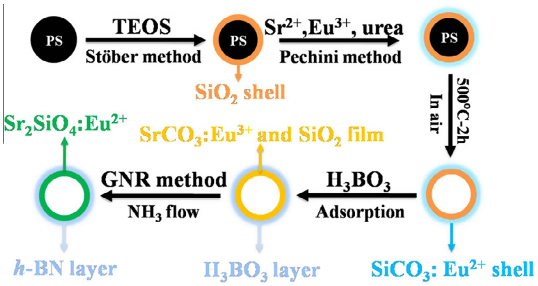
The morphology of the core–shell samples was investigated using a scanning electron microscope (SEM), which is equipped with a back scattered electron image (BSEI) (JEOL-6390LA, JEOL, Japan). The Energy Dispersive X-ray Spectrdmeter EDS and inductively coupled plasma atomic emission spectromemer (ICP-AES) (Optima 7300DV, Perkin Elmer Corporation, USA) were used to analysis the elements of the core–shell structure. The core–shell structure was investigated using the high resolution transition electron microscopy (HR-TEM) (JEOL-2010, JEOL, Japan).

The photoluminescence spectra were measured at room temperature by a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Japan) with a 200 W Xe-lamp as an excitation source. The emission spectrum was corrected for the spectral response of a monochromator and Hamamatsu R928P photomultiplier tube (Hamamatsu Photonics K.K., Hamamatsu, Japan) by a light diffuser and tungsten lamp (Noma Electric Corp., NY; 10 V, 4 A). The excitation spectrum was also corrected for the spectral distribution of the xenon lamp intensity by measuring Rhodamine-B as references.

3. Results and discussion

3.1. Phase, structure and elementary composition of the hollow spherical Sr_2SiO_4:Eu^{2+} phosphor

Fig. 1 shows the XRD pattern of the as-received spherical hollow Sr_2SiO_4:Eu^{2+} phosphor and the JCPDS 76-1494 card for Sr_2SiO_4 as



Scheme 1. The schematic fabrication processes of the hollow spherical Sr_2SiO_4:Eu^{2+} phosphors.