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Uniform and well-dispersed Y_2O_3:Eu/YVO_4:Eu composite microspheres with high photoluminescence prepared by chemical corrosion approach

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ABSTRACT

Uniform and well-dispersed Y_2O_3:Eu/YVO_4:Eu composite microspheres were prepared by hydrothermal chemical corrosion Y_2O_3:Eu microspheres with Na_3VO_4 solution. Effects of pH, molar ratio of Na_3VO_4 to the Y_2O_3:Eu precursor (R), and reaction time (t) on the morphology and the crystal structure of the composite were investigated in detail. The photoluminescence intensity of the products synthesized under the optimum condition was much higher than that of the YVO_4:Eu nanocrystals prepared by direct hydrothermal method and comparable to that of the bulk YVO_4:Eu.

1. Introduction

Bulk Eu^{3+}-activated YVO_4:Eu is an important commercial red phosphor widely used in color television, cathode ray tube and high-pressure mercury lamp owning to the efficient energy transfer from VO_4^{3-} to Eu^{3+}, high luminescence quantum yields (~70%) and superior chromaticity (stronger $^5D_0$ to $^7F_2$ transition) [1,2]. Bulk YVO_4:Eu is normally prepared by solid-state reaction at temperatures above 1200 K. However, it is difficult to control the homogeneity, morphology and size of the final products by this method [3].

The increasing demands for high brightness, resolution and efficiency in phosphors for field emission displays and cathode ray tube have promoted the exploration of phosphors with spherical or nearly spherical shape, narrow size distribution (<2 μm), and non-aggregation [4,5]. Thus far, many efforts have been devoted to prepare YVO_4:Eu nano- or microspheres. For example, Yu et al. explored a kind of core–shell-structured SiO_2@YVO_4:Eu phosphor with uniform and monodispersed spherical morphology by a sol–gel method [6]. In another report, uniform, monodispersed and size-controllable YVO_4:Eu nano- or microspheres were synthesized by a solvothermal method [7]. However, the luminescence efficiency of the products obtained by these methods is much lower than that of corresponding bulk materials due to nonradiative relaxation originating from surface recombination, surface defects and surface electronic states in the nanophosphors [8–10].

Recently, chemical corrosion has been proven to be an effective approach to prepare heterostructure composite with improved properties or some new functions [11–15]. Uniform and monodispersed $YOHCO_3$:Eu microspheres could be easily prepared by urea-based homogeneous precipitation technique and transformed into Y_2O_3:Eu microspheres after calcination [16]. Here, we successfully prepared uniform and well-dispersed Y_2O_3:Eu/YVO_4:Eu composite microspheres by hydrothermal chemical corrosion the Y_2O_3:Eu precursor with Na_3VO_4 solution and investigated the synthetic conditions including the pH, the molar ratio of Na_3VO_4 to the Y_2O_3:Eu precursor (R), and the reaction time (t) on the morphology and the crystal structure of the composite. This novel composite exhibited much higher photoluminescence than the YVO_4:Eu nanocrystals prepared by direct hydrothermal process, which might have potential applications in field emission displays or lighting devices.

2. Materials and methods

2.1. Materials

All reagents used were analytical grade without further purification. $Y(NO_3)_3$ and $Eu(NO_3)_3$ aqueous solutions were obtained by dissolving Y_2O_3 (99.99%) and Eu_2O_3 (99.99%) in dilute HNO_3 solution.

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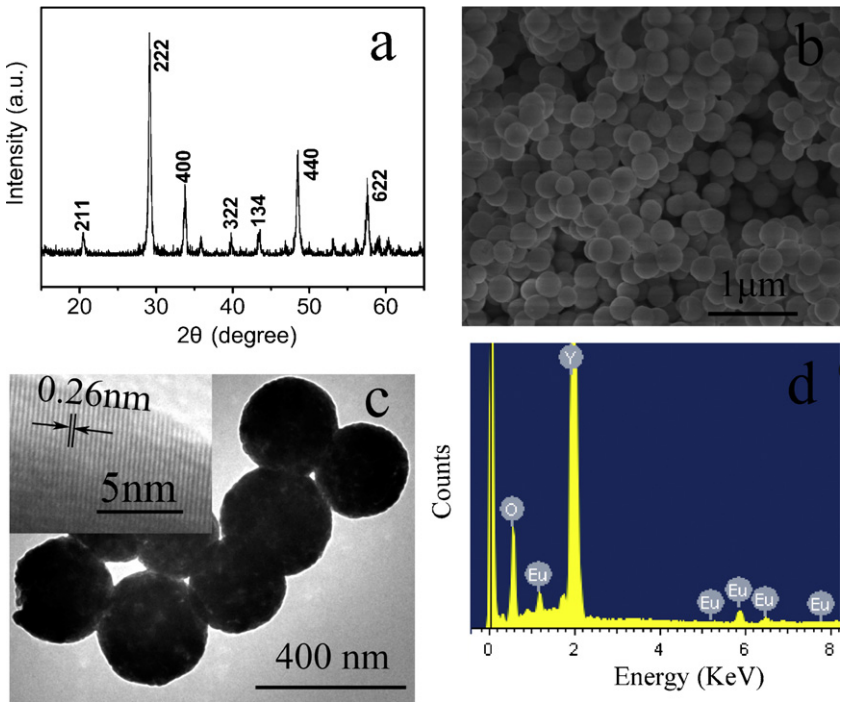

Fig. 1. Characterization of the Y_2O_3:Eu precursor. (a) XRD pattern; (b) SEM image; (c) TEM and HRTEM images; (d) EDX spectrum.

2.2. Synthesis of Y_2O_3:5%Eu colloidal spheres

$YOHCO_3$:Eu microspheres were prepared according to the previous report with modification [17]. Briefly, 20 mmol urea was dissolved in 100 ml distilled water, and then a solution contained 1.9 mmol $Y(NO_3)_3$ and 0.1 mmol $Eu(NO_3)_3$ were dropped into the urea aqueous solution. After magnetic stirring for 1 h, the mixed solution was heated at 90 °C for 3 h in an oil bath. The products were washed with deionized water for 3 times, dried in an oven at 80 °C for 6 h and then calcinated in a muffle furnace at 700 °C for 2 h.

2.3. Synthesis of Y_2O_3:Eu/YVO_4:Eu composite microspheres

In a typical process, 0.04 g NH_4VO_3 (R = 20%) was added into 20 ml deionized water, and then the pH value was adjusted to 12 using 2 M NaOH solution. 0.1 g Y_2O_3:Eu precursor was dispersed in the solution by sonication for 30 min. The suspension was transferred to a 25 ml autoclave and heated at 180 °C for 5 h. After cooling, the products were collected, washed with deionized water for 3 times and then dried at 80 °C for 6 h.

2.4. Synthesis of YVO_4:5%Eu nano- and micro-crystals

For comparison, well-crystallized YVO_4:Eu nanocrystals were prepared by one-step hydrothermal process. 1.9 mmol $Y(NO_3)_3$ and 0.1 mmol $Eu(NO_3)_3$ were mixed in 15 ml H_2O, and then 2 mmol NH_4VO_3 was added. The pH value was adjusted to 12 using 2 M NaOH solution. The suspension was transferred to a 25 ml autoclave and heated at 180 °C for 12 h. Bulk YVO_4:Eu was prepared by solid state reaction of Y_2O_3, Eu_2O_3, and V_2O_5 with stoichiometric ratio at 1100 °C for 6 h.

2.5. Characterization

X-ray diffraction (XRD) patterns of the powder were recorded on a Bruker/D8-advance with Cu Kα radiation (λ = 1.54178 Å). Scanning electron microscopy (SEM) images were taken with a Hitachi FESEM-4800 field emission microscopy equipped with a Horiba EX-450 energy-dispersive X-ray (EDX) spectroscopy. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) analysis were examined by a JEOL JEM-2100 TEM (Japan). The elemental analysis was tested on an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Thermo Electron IRIS Intrepid II XSP, USA). The X-ray photoelectron spectra (XPS) were taken on a Thermo ESCALAB 250 electron energy spectrometer using Al Kα (1486.6 eV) as the Mono X-ray excitation source. Excitation and emission spectra of the samples were measured by an F-4500 phosphorimeter using a 450 W xenon lamp as excitation source.

3. Results and discussion

3.1. Characterization of the Y_2O_3:Eu precursor

XRD pattern (Fig. 1a) reveals the Y_2O_3:Eu precursor is well-crystallized and pure single-phased. All the diffraction peaks can be well indexed to the cubic Y_2O_3 (JCPDS file no. 65-3178). SEM and TEM images (Fig. 1b and c) show that the Y_2O_3:Eu precursor is consisted of highly uniform and mono-dispersed microspheres with a narrow size-distribution in the range of 250–300 nm. The well-defined lattice fringes with interplanar spacing of 0.26 nm can be clearly seen in the HRTEM image inserted in Fig. 1c, which can be ascribed to the (4 0 0) lattice plane of the cubic Y_2O_3. The EDX spectrum (Fig. 1d) clearly confirms the presence of Y, O, Eu in the Y_2O_3:Eu precursor.

3.2. Characterization of the Y_2O_3:Eu/YVO_4:Eu composite microspheres

The SEM and TEM images (Fig. 2a–c) clearly show the spherical morphology and the size of the composite obtained by chemical corrosion are almost unchanged. The surface of the composite mainly consists with small tetragon-like nanocrystals. XRD pattern