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One-dimensional hollow SrS nanostructure with red long-lasting phosphorescence

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Abstract

A novel one-dimensional (1D) hollow nanostructure of SrS:Eu^{2+}, Dy^{3+} with red long lasting phosphorescence was successfully fabricated by a soft template method followed by annealing treatment at 900 °C. The 1D nanostructures are 60–100 nm in diameter and several hundreds nanometers in length. The TEM image indicates that the 1D nanostructure could be considered to be assembled in lines by lots of nano-hollow spheres. The properties of photoluminescence and afterglow of the 1D nanostructure were also investigated and discussed.

Keywords: Nanostructured materials; Phosphors; Chemical synthesis; Optical properties; Luminescence

1. Introduction

As an important Lenard phosphor, SrS, a member of alkaline-earth sulfide with bandgap of 4.30 eV, has obtained great attention due to the potential for applications in infrared sensors, X-ray radiation imaging plates, optical storage media and full-color electroluminescent (EL) devices [1–5]. To obtain different luminescent properties, various elements, such as Eu, Sm, Pr, Ce and Cu, are doped in SrS. Among these, Eu^{2+} doped SrS is considered to be the most promising candidate for red phosphor. Meanwhile, Eu^{2+}, Dy^{3+} co-doped SrS is a red long-lasting phosphor, which can store to release the energy of absorbing light as photoluminescence [6,7]. Despite low dimensional nanostructures are of importance in nanodevices [8–11], only two-dimensional SrS films have been grown by different methods, such as metal-organic chemical vapor deposition [12], molecular-beam epitaxy (MBE) [13], atomic layer deposition [14], electron beam evaporation [15] and pulse laser deposition (PLD) [3] methods, evaporation/co-evaporation methods [16,17]. The one-dimensional nanostructure of SrS phosphors has not yet been realized so far. In addition, due to the instability of SrS in solution, so far, there are few reports on these nanostructures obtained directly or indirectly by wet methods.

In this paper, we report, a new kind of 1D hollow nanostructure of SrS:Eu^{2+}, Dy^{3+} with red long-lasting phosphorescence properties. which was fabricated by combining the soft template method of arranging CS_2 oil drops in lines with post-annealed treatment in Ar and H_2 atmosphere. The XRD result indicate the SrS structure of the product, and the SEM and HRTEM reveal the one-dimensional structure constructed by lots of voids in the center. We also investigate and discuss the properties of photoluminescence and long-lasting phosphorescence. The materials we obtained are envisaged to have significant implications in display devices and biolabeling applications. In addition, the nanoscale phosphor has the great commercial value.

2. Experimental details

The fabricating process of 1D hollow nanostructure of SrS:Eu^{2+}, Dy^{3+} is shown as follows. The commercial powders of 0.1 mol $Sr(NO_3)_2$, 0.003 mol $Eu(NO_3)_3$ and 0.003 mol $Dy(NO_3)_3$ were mixed with 50 ml de-ions water in a conical flask. After 30 min stirring, 2 g sodiumsalt dodecyl benzene sulfonic acid (SDBS), 2 ml CS_2 and appropriately butanol were added into. Six hours later, the ammonium oxalate saturation solution was then added dropwise into the solution while keeping stirring. Precipitates occurred and then the emulsion

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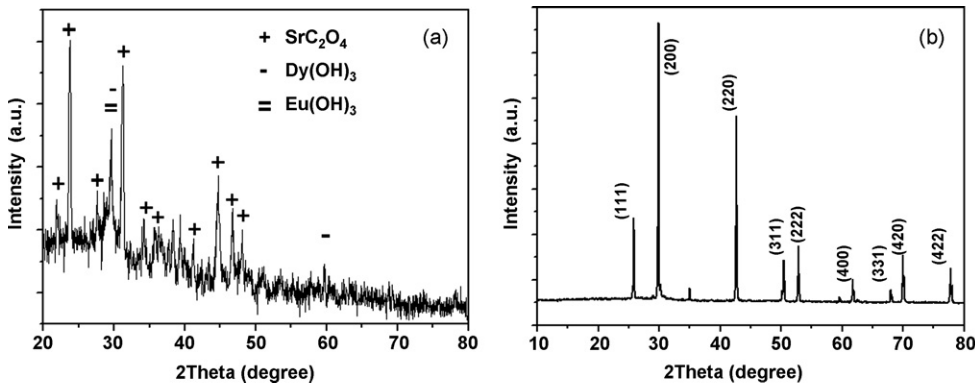

Fig. 1. XRD patterns. (a) Precipitated products; (b) the final 1D SrS:Eu^{2+}, Dy^{3+} nanostructure obtained by annealed at 900 °C for 2 h.

was filtrated. The obtained product was washed several times with de-ions water and ethanol to remove the excessive surfactant and other remnants. Finally, the above product was annealed at 900 °C for about 2 h in flowing 95% Ar and 5% H_2 atmosphere.

The characterization experiments of the samples were carried out at room temperature. Phase identification of the powders was carried out by X-ray diffraction (XRD) using a Philips X'Pert Pro MPD with Cu Kα (λ = 1.5406 Å) radiation. The morphological investigation was carried out using high resolution transmission electron microscopy (HRTEM; JEOL JEM-2010, 200 kV) and field emission scanning electron microscopy (FESEM; FEI Sirion-200). Photoluminescence (PL) spectra were obtained using a photoluminescence spectrometer (Edinburgh FLS 920). The decay curves of the afterglow were measured by a ST-900 photometer after the samples irradiated by Hg lamp with the wavelength of 365 nm and the intensity of 6 mW cm^{-2} for 10 min.

3. Results and discussion

Representative XRD patterns of precipitated and post-annealed samples are shown in Fig. 1. The diffraction peaks of the precipitated product are complicated (in Fig. 1(a)), which mainly arise from strontium oxalate hydrate (JCPDS card of 191281), and the peaks of europium hydroxide (JCPDS card of 170781) and dysprosium hydroxide (JCPDS card of 832039) also appear in the patterns. After annealed at 900 °C for about 2 h in flowing 95% Ar and 5% H_2 atmosphere, all of the diffraction peaks can be neatly indexed to face center cubic symmetry structure SrS (JCPDS card of 75-0895, space group of *Fm*3*m*) (in Fig. 1(b)). The diffraction peaks related to Eu and Dy disappeared, indicating that the Eu and Dy have incorporated into SrS host lattice.

The FESEM characterization of the final product is shown in Fig. 2, which shows a characteristic fibrous morphology. The product has length in about several hundred nanometers. The typical TEM image of the 1D nanostructure is shown in Fig. 3. The 1D nanostructures are 60–100 nm in diameter, and they are assembled by lots of nano-globose cells which may be the spaces left by CS_2 droplets after annealing. The selected area electron diffraction (SAED) pattern (insert in Fig. 3(a)) presents diffuse polycrystalline rings. This is consistent with the result shown in the high-resolution TEM image (Fig. 3(b)). The 1D nanostructure is composed of lots of different small grains. The fast Fourier transform (FFT) and the invert fast Fourier transform (IFFT) analyses of an individual particle HRTEM image were inset in Fig. 3(b). The lattice planes with interplanar spacing of 0.425 nm is clearly displayed, which matches well with (1 1 0) planes of the standard bulk SrS. The compositions of the 1D hollow nanostructures were analyzed by energy-dispersive spectra (EDS). The results indicate that they are composed of Sr, S, Eu and Dy elements (insert in Fig. 3(a)).

The growth mechanism of the 1D hollow nanostructure of SrS:0.03Eu^{2+}, 0.03Dy^{3+} can be proposed as follows. The oil droplets of CS_2 in the solution are enwrapped by SDBS firstly (Fig. 4, step a). After that, excess surfactant can arrange these CS_2 micells in lines which can be served as the reaction template (Fig. 4, step b). When the ammonium oxalate saturation solution was added into the solution, strontium oxalate hydrate occurred and aggregated on the surface of the complex template, and the oil drops of CS_2 were enwrapped by the precipitates (Fig. 4, step c). So, the 1D hollow usher has been fabricated. Finally, when annealing at 900 °C for about 2 h in flowing 95% Ar and 5% H_2 atmosphere (Fig. 4, step d), the oil drops of CS_2 were vaporized and the precipitates were vulcanized. As a result, 1D hollow nanostructure of SrS:Eu^{2+}, Dy^{3+} was obtained.

The optical emission spectrum at room temperature is shown in Fig. 5(a). The nanostructured sample was illuminated with 460 nm light. There is only one red broadband emission peak

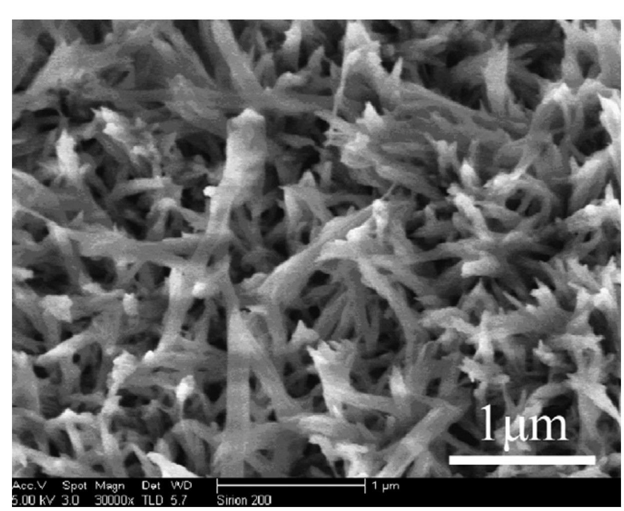

Fig. 2. The FESEM image of the 1D hollow SrS:Eu^{2+}, Dy^{3+}nanostructure.

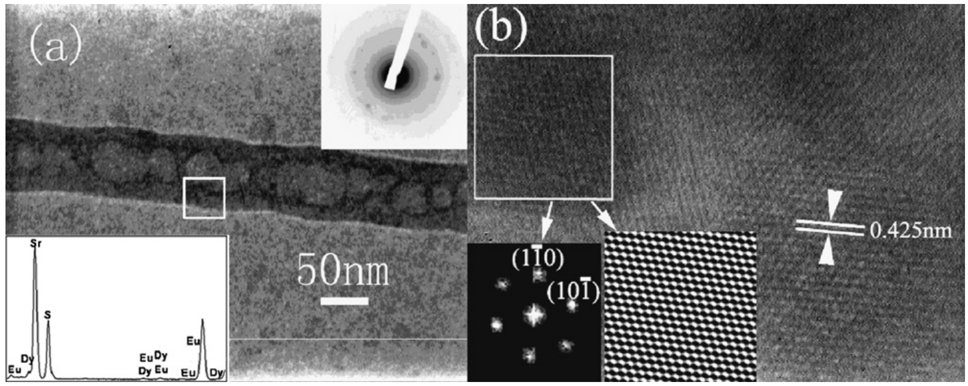

Fig. 3. TEM imagies of SrS:Eu^{2+}, Dy^{3+} 1D hollow nanostructure. (a) The TEM pattern of single 1D nano hollow structure, the upper and lower inserts in (a), corresponding SAED pattern and the EDS spectrum of the nanostructure. (b) Magnified image of the side part of the 1D nanostructure, the insets in (b) show FFT (left) and IFFT (right) analyses obtained from corresponding areas in the crystal (outlined).

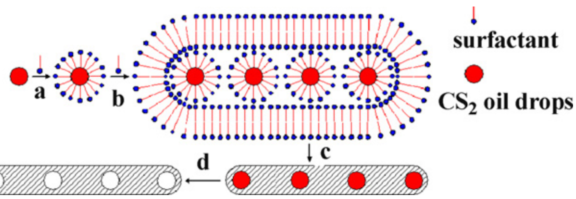

Fig. 4. The schematic of fabricating 1D SrS:Eu^{2+}, Dy^{3+} hollow nanostructure. (a) CS_2 oil droplets was enwrapped by the surfactant. (b) The former was arranged by the excess surfactant. (c) Precipitates occurred and aggregated on the surface of the complex template. (d) The product was annealed in Ar and H_2 atmosphere at 900 °C for 2 h.

centered at 607 nm, which can be attributed to the electronic transition ($4f^65d^1 \rightarrow 4f^7$) of Eu^{2+} ions occupied cation sites in SrS phosphor [2]. The special emission of Dy^{3+} did not occur in the pattern, which indicated that the Dy^{3+} ions in the phosphor serve not as the luminescent centers. Fig. 5(b) gives the excitation spectrum of the 1D hollow-nanostructure sample monitored at 607 nm. They both have two broad excitation bands in the range of 250–570 nm centered at about 275 nm and 460 nm, respectively. The peak center at about 275 nm arises from the band-to-band transition in SrS, and the peak center at about 460 nm arises from the ($4f^7 \rightarrow 4f^65d^1$) electronic transition of Eu^{2+} ions [2]. On the long wavelength band which centered at 460 nm, there are seven sub-peaks centered at about 495, 490, 475, 470, 465, 459, and 455 nm, marked as 1–7 in the Fig. 5(b), respectively. These sub-peaks are corresponded to the well-known electronic transitions between the splitted $4f^65d$ configuration and the ground state of $4f^7$ of Eu^{2+} ions [18]. Fig. 6 gives the decay curves of the long-lasting phosphorescence. The mechanism of the long-lasting phosphorescence is sophisticated. An explanation could be put forward as followed. In the weak reductive atmosphere as post annealed treatment, a lot of defect energy-level appeared. Some are electrons trap, such as the vacancies of S^{2-}. Others are holes trap, such as Dy^{3+} or the vacancies of Sr^{2+} [19]. After stimulating by light, electrons in the 4f energy-level of Eu^{2+} ions could transmit to the 5d energy-level and leaving holes in the valence band [20]. The holes transport in valence band could be captured by the holes trap, and electrons transport in conducting band could also be captured by the electron traps. The holes and electrons in traps could be released by thermal activation process, respectively. The electrons recombine with holes in the excited state of Eu^{2+} ions, and the excited electrons could return to the ground state of $4f^7$ with visible light emitting. For the slowing process of the holes and electrons releasing in traps, the phosphor exhibits long-lasting phosphorescence.

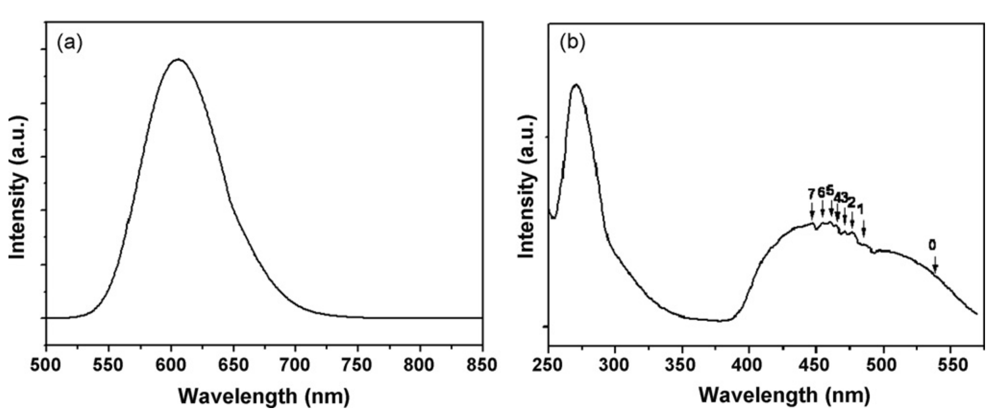

Fig. 5. (a) The room temperature emission spectrum. (b) The room temperature excitation spectrum of the 1D hollow SrS:Eu^{2+}, Dy^{3+}nanostructure.

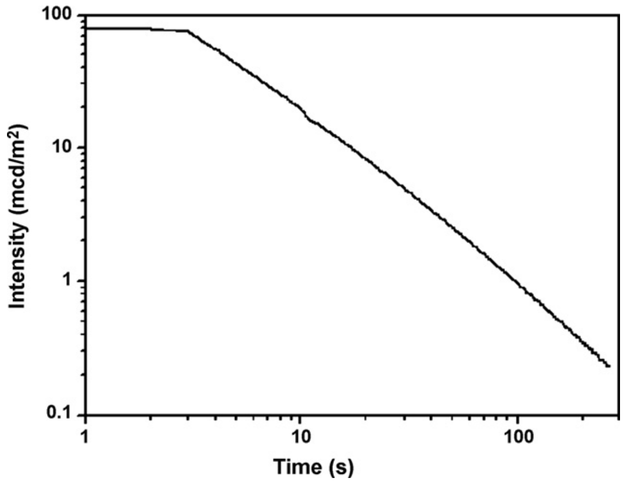

Fig. 6. The decay curve of afterglow of the 1D hollow $SrS:Eu^{2+}$, Dy^{3+} nanostructure.

4. Conclusion

In summary, a novel lD hollow nanostructure of $SrS:Eu^{2+}$, Dy^{3+} with red long-lasting phosphorescence was synthesized via a soft template method followed by post-annealing. This novel structure can be considered to be assembled in lines by lots of nano-hollow spheres and the synthetic procedure can be applied to the fabrication of some other complex materials with the similar structures. Moreover, the 1D hollow nanostructure of $SrS:Eu^{2+}$, Dy^{3+} provides a potential application as micromarkers in future nanodevices and as fluorescent probes in biological fields.

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